



**UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ**

**FACULTAD DE CIENCIAS QUÍMICAS**

**Centro de Investigación y Estudios de Posgrado**

**Posgrado en Ciencias en Ingeniería Química**



**UNIVERSIDAD DE GRANADA**

**FACULTAD DE CIENCIAS**

**Departamento de Química Inorgánica**

**Programa de Doctorado en Química**

**Adsorción de compuestos farmacéuticos en solución  
acuosa sobre arcillas naturales y nanomateriales de  
carbono**

Tesis en cotutela internacional que para obtener los grados de:

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por la Universidad Autónoma de San Luis Potosí

**Doctor en Química**

por la Universidad de Granada

Presenta:

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**Dr. Roberto Leyva Ramos**

**Dr. Francisco Carrasco Marín**

SAN LUIS POTOSÍ, S. L. P.

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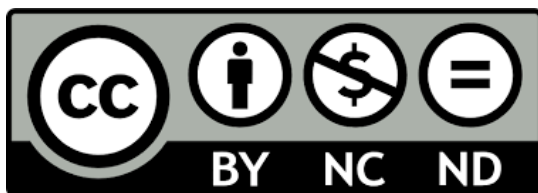
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La primera parte de la tesis doctoral se realizó en el Laboratorio de Ingeniería Química Ambiental perteneciente a la Facultad de Ciencias Químicas de la Universidad Autónoma de San Luis Potosí (México), en el periodo comprendido entre agosto 2020 y julio 2022, bajo la dirección del Dr. Roberto Leyva Ramos. La segunda parte de la tesis doctoral se llevó a cabo en el grupo de investigación Materiales Polifuncionales Basados en Carbono (UGR-Carbon) perteneciente a la Facultad de Ciencias de la Universidad de Granada (España), en el periodo comprendido entre agosto 2022 y julio 2024, bajo la dirección del Dr. Francisco Carrasco Marín. Este trabajo de investigación ha sido financiado por la Asociación Universitaria Iberoamericana de Postgrado, España con la beca de movilidad *PMA2-2022-123-14* en Andalucía – Segundo Plazo 2022, la Consejería de Universidad, Investigación e Innovación (Junta de Andalucía) 2021-2027 por el proyecto *C-EXP-247-UGR23*, el Ministerio de Ciencia e Innovación / Agencia Estatal de Investigación / 10.13039/501100011033 y el Fondo Europeo de Desarrollo Regional Una manera de hacer Europa por el proyecto *PID2021-127803OB-I00*



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**Agosto, 2024**

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Sin más por el momento, le envío un cordial saludo.

**A T E N T A M E N T E**

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Dr. Erik César Herrera Hernández  
Coordinador Académico del Posgrado  
en Ciencias en Ingeniería Química

*“A bit of science distances one from God,  
but much science nears one to him”*

**Louis Pasteur**

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## Resumen

Este trabajo se centra en el desarrollo de materiales basados en arcillas naturales y en la fabricación de estructuras monolíticas de carbono con porosidad y geometrías de canales controladas por impresión 3D, aplicados para eliminar contaminantes farmacéuticos del agua. Se estudió la adsorción de tetraciclina, trimetoprima y clorfenamina en varias arcillas, destacando la bentonita por su alta capacidad de adsorción gracias a su estructura laminar y propiedades de hinchamiento. La adsorción de trimetoprima y tetraciclina está gobernada por difusión superficial, y la de clorfenamina por difusión en el volumen del poro. En la adsorción binaria de tetraciclina y cadmio se encontraron efectos competitivos y sinérgicos en función del pH de la solución. La organobentonita híbrida mostró altas capacidades de adsorción según la carga iónica y naturaleza hidrofóbica del fármaco. Los resultados indicaron que las interacciones electrostáticas son el principal mecanismo de adsorción y que la velocidad de adsorción se debe al transporte externo de masa.

Se diseñaron y fabricaron innovadores adsorbentes monolíticos de carbono con diferentes texturas porosas y geometrías avanzadas de canales mediante impresión 3D. Las variables de síntesis analizadas incluyeron la relación resorcinol/catalizador, el agente activante ( $\text{CO}_2$  y  $\text{H}_2\text{O}$ ), tiempos de activación y geometrías de canales. Estas variables se evaluaron en la adsorción de sulfametoxazol. Los monolitos de carbono mostraron una integración óptima de alta resistencia mecánica con geometrías de canales avanzadas controladas y replicadas fielmente por la impresión 3D, con una macroestructura porosa de baja resistencia al flujo. Las variables de síntesis afectaron significativamente la morfología, logrando una estructura porosa jerárquica con alta área superficial, superando la capacidad de adsorción de muchos materiales adsorbentes existentes. Las geometrías de canales influyeron drásticamente en las curvas de ruptura: monolitos de canales rectos, hexagonales y romboidales tuvieron tiempos de ruptura tempranos por efectos de canalización, mientras que los de red interconectada mostraron mayores tiempos de ruptura, mitigando estos efectos gracias a la turbulencia y mezclado, confirmados por simulaciones CFD.

**Palabras clave:** adsorción, fármacos, arcillas, monolitos de carbono, impresión 3D.

## **Abstract**

This work focuses on the development of clay-based materials and the fabrication of carbon monolithic structures with controlled porosity and channel geometries using 3D printing, aimed at removing pharmaceutical contaminants from water. The adsorption of tetracycline, trimethoprim and chlorphenamine on various clays was studied, with bentonite showing high adsorption capacity due to its laminar structure and swelling properties. The adsorption of trimethoprim and tetracycline is governed by surface diffusion, while chlorphenamine adsorption is controlled by pore volume diffusion. Binary adsorption of tetracycline and cadmium revealed competitive and synergistic effects depending on solution pH. Hybrid organobentonite exhibited high adsorption capacities based on the ionic charge and hydrophobic nature of the drug. Results indicated that electrostatic interactions are the primary adsorption mechanism, and that adsorption rate is due to external mass transport.

Innovative carbon monolithic adsorbents with different porous textures and advanced channel geometries were designed and fabricated using 3D printing. The synthesis variables analyzed included resorcinol/catalyst ratio, activating agents ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ), activation times and channel geometries. These variables were evaluated in sulfamethoxazole adsorption. Carbon monoliths showed optimal integration of high mechanical strength with advanced channel geometries, faithfully replicated by 3D printing, and a porous macrostructure with low flow resistance. Synthesis variables significantly affected morphology, achieving a hierarchical porous structure with high surface area, surpassing the adsorption capacity of many existing adsorbent materials. Channel geometries drastically influenced breakthrough curves: monoliths with straight, hexagonal and rhomboidal channels had early breakthrough times due to channeling effects, while interconnected network channel showed longer breakthrough times, mitigating these effects through turbulence and mixing, confirmed by CFD simulations.

**Keywords:** adsorption, pharmaceuticals, clays, carbon monoliths, 3D printing.

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# CHAPTER

**THESIS STRUCTURE,  
PUBLICATIONS AND  
CONFERENCES**

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In this thesis, clay-based materials and carbon monolithic structures with controlled porosity and channel geometries developed using an innovative method that combines sol-gel polymerization with 3D printing technology, were designed for the removal of pharmaceutical compounds from water through adsorption processes. The experimental results and their discussion are presented in twelve chapters.

**Chapter 1** discusses the environmental issues caused by water contamination from emerging contaminants, particularly pharmaceutical compounds, highlighting the importance of effectively removing these contaminants from water. Possible treatment methods, such as adsorption, are also discussed, and hypotheses are proposed regarding the development of clay-based materials and monolithic structures as promising materials that can address this environmental problem.

**Chapter 2** provides an extensive background of the research and compiles data on pharmaceutical contaminants most commonly detected in water systems and their concentrations. Additionally, it discusses materials that have been studied in the literature for the adsorption of these contaminants, emphasizing the importance of developing novel materials based on natural clays and carbon materials, which have been poorly studied in the literature compared to conventional adsorbents. The chapter also outlines the objectives of the thesis.

**Chapter 3** describes the experimental methods used in this thesis.

**Chapter 4** focuses on investigating the effect of structural characteristics of several clays, such as bentonite, sepiolite, vermiculite, halloysite, phlogopite and kaolinite, on the adsorption of tetracycline from water. The chapter explores how varying operating conditions such as pH, ionic strength and temperature influence the adsorption mechanisms.

**Chapter 5** investigates the influence of the textural, chemical and swelling properties of bentonite on the adsorption of trimethoprim and chlorphenamine. Samples of bentonite saturated with varying amounts of these pharmaceuticals were prepared and characterized using several techniques to explore these physicochemical properties of bentonite affecting adsorption capacities. Reversibility studies were also conducted to assess the reusability of the clay.

**Chapter 6** implemented the External Mass Transport model, Pore Volume Diffusion Model and Pore Volume and Surface Diffusion Model to analyze the adsorption kinetics of trimethoprim, tetracycline and chlorphenamine in aqueous solution on natural bentonite clay. The influence of operational parameters such as initial concentration and stirring speed was examined to elucidate mass transfer mechanisms. Additionally, the dependence of mass transport parameters on the uptake adsorbed at equilibrium was analyzed.

**Chapter 7** analyzes the simultaneous adsorption of tetracycline and cadmium (II) using 2:1 layered clays under different operating conditions, emphasizing the efficacy of clay materials in removing both organic and inorganic contaminants simultaneously. Multicomponent adsorption isotherm models were employed to satisfactorily fit the binary adsorption data surfaces, and the materials loaded with adsorbed tetracycline and cadmium (II) were characterized to elucidate the mechanisms of binary adsorption.

**Chapter 8** explores the synthesis of a hybrid hexadecyltrimethylammonium bromide-modified organobentonite and its efficacy in adsorbing various pharmaceutical compounds with different ionic properties, such as chlorphenamine, sulfamethoxazole, tetracycline and carbamazepine. Organobentonite was prepared using a cation exchange reaction route and extensively characterized through several techniques. The study evaluates the impact of operating conditions on adsorption isotherms and delves into the mass transfer mechanisms governing the adsorption rates on organoclays.

**Chapter 9** is dedicated to the synthesis of pellet-type carbon xerogel adsorbents for the efficient removal of sulfamethoxazole from water using sol-gel polymerization processes. The effect of synthesis conditions on the chemical, textural, morphological and mechanical properties of the xerogels was evaluated by preparing materials with different resorcinol/catalyst ratios. The adsorption capacities of these materials were assessed under various conditions, including pH, ionic strength and temperature.

**Chapter 10** proposes a novel method combining sol-gel polymerization with advanced 3D printing technology to prepare 3D-printed carbon monolith adsorbents.

These adsorbents, featuring varied porous textures and designed channel geometries, are applied in the dynamic adsorption of sulfamethoxazole from water, representing a pioneering effort in the field. The impact of fabrication conditions was evaluated to produce carbon monoliths with high accessible macroporosity, low flow resistance and high-strength structures. The performance of these monoliths was characterized in both batch and continuous systems, assessing their effectiveness as monolithic beads.

**Chapter 11** engineers 3D-printed monolithic activated carbons from CO<sub>2</sub> and H<sub>2</sub>O using combined method of sol-gel polymerization with 3D printing technology. Four distinct 3D CAD prototypes were designed to represent various channel geometries. The effect of activating agents and activation times was evaluated on the textural and morphological properties, adsorption isotherms and breakthrough curves. Finally, the impact of channel geometry on dynamic breakthrough curves was analyzed and corroborated by Computational Fluid Dynamics (CFD) calculations.

**Chapter 12** presents overall conclusions drawn from this research. This chapter summarizes the key achievements and highlights the potential applications of the developed materials.

The research work presented in this doctoral thesis resulted in the following publications in high-impact journals and book chapters:

- U. Ortiz-Ramos, R. Leyva-Ramos, E. Mendoza-Mendoza, A. Aragón-Piña. *Removal of tetracycline from aqueous solutions by adsorption on raw Ca-bentonite. Effect of operating conditions and adsorption mechanism.* Chemical Engineering Journal, 432 (2022) 134428. *JIF = 16.744, Q1*
- U. Ortiz-Ramos, R. Leyva-Ramos, E. Mendoza-Mendoza, F. Carrasco-Marín, E. Bailón-García, D. E. Villela-Martínez, G. D. Valdez García. *Modeling adsorption rate of trimethoprim, tetracycline and chlorphenamine from aqueous solutions onto natural bentonite clay. Elucidating mass transfer mechanisms.* Chemical Engineering Journal, 493 (2024) 152666. *JIF = 15.1, Q1*



- U. Ortiz-Ramos, E. Bailón-García, A. F. Pérez-Cadenas, R. Leyva-Ramos, F. Carrasco-Marín. *Synthesis of porous carbon xerogel adsorbents with tailored hierarchical porosity and morphology for the selective removal of sulfamethoxazole from water*. Submitted to Science of the Total Environment, (2024). JIF = 8.2, Q1
- R. Leyva-Ramos, D. E. Villela-Martínez, U. Ortiz-Ramos, G. D. Valdez-García, I. Ortiz-Anaya, D. H. Carrales-Alvarado. *Fundamentos de cinética de adsorción en sistemas líquido-sólido. Desarrollo y aplicación de modelos difusionales*. In book: Fundamentos de adsorción aplicados a la eliminación de compuestos tóxicos presentes en solución acuosa. Chapter: 7, Ediciones Uniandes (2024).

Additionally, the following research publications are currently in progress:

- U. Ortiz-Ramos, R. Leyva-Ramos, E. Mendoza-Mendoza, F. Carrasco-Marín. *Impact of chemical, textural and swelling properties of bentonite clay on its adsorption capacity for trimethoprim and chlorphenamine in aqueous solutions*.
- U. Ortiz-Ramos, R. Leyva-Ramos, E. Mendoza-Mendoza, F. Carrasco-Marín. *Competitive and cooperative binary adsorption of tetracycline and cadmium (II) onto 2:1 layered calcium bentonite clay from aqueous solutions*.
- U. Ortiz-Ramos, R. Leyva-Ramos, E. Mendoza-Mendoza, F. Carrasco-Marín. *Exploring adsorptive behavior of cationic, anionic, zwitterionic and neutral pharmaceuticals in aqueous solution on hexadecyltrimethylammonium bromide-modified organobentonite*.
- U. Ortiz-Ramos, E. Bailón-García, A. F. Pérez-Cadenas, R. Leyva-Ramos, F. Carrasco-Marín. *Advanced design and fabrication of new 3D-printed carbon monolith adsorbents for the removal of sulfamethoxazole from water: Effect of synthesis conditions on their dynamic adsorption performance*.

- U. Ortiz-Ramos, E. Bailón-García, A. F. Pérez-Cadenas, R. Leyva-Ramos, F. Carrasco-Marín. *3D-printed monolithic activated carbons for the dynamic sulfamethoxazole adsorption from water: Influence of activation time on adsorption capacity and breakthrough curves.*
- U. Ortiz-Ramos, E. Bailón-García, A. F. Pérez-Cadenas, R. Leyva-Ramos, F. Carrasco-Marín. *Optimizing fluid dynamics and adsorption breakthrough curves: Impact of advanced CAD-designed channel geometries in 3D-printed carbon monoliths for sulfamethoxazole removal from water.*

Most of these results were presented at the following national and international conferences:

- Simposio Virtual: Nanotecnología y sus Aplicaciones en el Área de la Química. *San Luis Potosi, Mexico, October 2020.*
- Foro sobre la Apropiación Social de Tecnologías para la Gestión Sostenible del Agua. *Puebla, Mexico, November 2020.*
- Pre-IV Workshop on Adsorption, Catalysis and Porous Materials. *Bogota, Colombia, October 2021.*
- AiChE Annual Meeting. *Massachusetts, United States of America, November 2021.*
- Primer Foro de Adsorción en México. *Nuevo Leon, Mexico, December 2021.*
- Primer Foro Estatal del Agua. *San Luis Potosi, Mexico, May 2022.*
- IV Workshop of Adsorption, Catalysis and Porous Materials. *Bogota, Colombia, November 2022.*
- I Jornada de Jóvenes Investigadores del Grupo Español del Carbón. *Baeza, Spain, December 2022.*
- V Simposio de la Unidad de Excelencia de Química. *Granada, Spain, January 2023.*
- 15th Mediterranean Congress of Chemical Engineering. *Barcelona, Spain, June 2023.*

- XVI Reunión del Grupo Español del Carbón. *Gijón, Spain, October 2023.*
- VI Simposio de la Unidad de Excelencia de Química. *Granada, Spain, January 2024.*

# CHAPTER

INTRODUCTION

1

Water is essential for life and ecosystems across the planet. It is the most important natural resource and also one of the most vulnerable. In recent years, the development of human activities has led to the emergence of new contaminants known as emerging contaminants (ECs). ECs include pharmaceutical compounds, personal care products, endocrine disruptors, dyes and agricultural chemicals. These contaminants can enter the environment through discharges of hospital, industrial and domestic wastewater. ECs are transported to wastewater treatment plants, continuously released into surface and groundwater systems, and detected in a wide range of concentrations, from ng/L to µg/L (Chaturvedi et al., 2021).

It is known that ECs can cause sexual disorders in marine organisms, neurological, reproductive and immunological alterations in animals, cancer, the development of antibiotic-resistant bacterial genes, and congenital heart disease, among other toxic effects (Gogoi et al., 2018). However, precise information on the toxic effects of ECs in water systems is limited.

One category of ECs that has gained priority is pharmaceuticals (Ahuja, 2021). Pharmaceuticals are widely used in the diagnosis, treatment, cure and prevention of various diseases in humans and animals due to their different physicochemical and biological properties. Most pharmaceuticals experience transformations in the body when ingested, resulting in the release of a large number of metabolites into surface and groundwater systems during wastewater treatment and cause irreparable harm to humans and ecosystems (Bexfield et al., 2019).

Currently, wastewater treatment plants play a crucial role in removing various contaminants, such as suspended particles, dissolved organic compounds, nutrients, and pathogens. These plants employ different treatment stages involving processes like sieving, coagulation/flocculation, centrifugation, sedimentation and biological treatments. However, current conventional technologies have limitations in reducing the concentrations of pharmaceutical compounds present in wastewater. To address this challenge, recent years have seen the development and implementation of more effective and specific treatment technologies. Among these technologies are methods

such as chlorination, ozonation, adsorption, advanced oxidation processes and visible light photodegradation.

Adsorption processes have been widely used and stand out as a promising and effective alternative for removing pharmaceuticals from wastewater. This technology offers a wide range of significant advantages, marking it an attractive option compared to other treatment techniques. Key advantages include ease of operation, low cost, reproducibility, high efficiency and the absence of toxic byproduct generation. Additionally, it offers flexibility in utilizing a wide range of adsorbent materials, from natural micrometric materials to advanced nanostructured synthetic materials (Cooney, 1998).

The aim of this thesis is to develop clay-based adsorbent materials and to fabricate nanostructured carbon monolith adsorbents with controlled porosity and channel geometries using 3D printing technology combined with sol-gel polymerization, both for the removal of pharmaceutical compounds from water. The study will focus on the effect of the chemical, textural and swelling properties of natural clays with distinct structural arrangements on the adsorption capacity of pharmaceutical compounds, as well as the impact of operational parameters on adsorption capacity. Furthermore, for the first time, the mass transport mechanisms controlling the overall adsorption rate of pharmaceutical compounds on natural clays will be elucidated by obtaining kinetic data under different experimental conditions.

In addition, hybrid materials will be prepared by intercalating organic molecules of cationic surfactants within the interlayer space of the clays to modify their surface chemistry and provide additional functional properties that enable the adsorption of pharmaceuticals in aqueous solution.

Furthermore, the fabrication of integral monoliths of carbon xerogels is proposed by combining sol-gel polymerization and 3D printing technology to be applied as adsorbents in continuous adsorption systems. The effect of synthesis conditions and channel geometry will be investigated to obtain monolithic structures with an appropriate and highly controlled chemical composition, porous structure and channel geometries for adsorption purposes.

# CHAPTER

**BACKGROUND OF THE  
RESEARCH AND OBJECTIVES**

# 2

## **2.1 Water contamination**

Water is essential for sustaining life and ecosystems worldwide, making it one of the most crucial yet vulnerable natural resources. Recent official figures estimate that each person consumes approximately 227 liters of water per day, contributing to the alarming rise of water pollution, a pressing global environmental concern (Vasilachi et al., 2021).

Water pollution can stem from both natural factors and various anthropogenic sources, including industrial dischargers, agricultural runoff, untreated sewage, oil spills, and chemical releases, among others. These pollutants can adversely impact water quality, aquatic ecosystems, and human health.

In recent years, human activities have given rise to the emergence of new organic pollutants known as “emerging contaminants”. This term is used when there is limited information available about the extent and frequency of the risks these contaminants pose to human health and the environment (Lofrano et al., 2020). Generally, emerging contaminants encompass a broad range of human-produced organic compounds considered essential for modern society but can pose long-term dangers to ecosystems and human health when present in water. According to the 2016 Global Burden of Diseases, Injuries, and Risk Factors Study (GBD), an estimated 1.3 million deaths were linked to 12 synthetic substances present in environment (Naghavi, 2017). In 2021, during the 5<sup>th</sup> United Nations Environment Assembly (UNEA5), environmental pollution was categorized as one of the top global challenges, alongside biodiversity loss and climate change. Consequently, it is evident that urgent action is required to address this global issue and implement effective measures to protect our ecosystems and ensure the health of future generations.

## **2.2 Emerging contaminants**

Emerging contaminants (ECs), as defined by the United States Geological Survey (USGS), are synthetic chemicals that are not regularly monitored in the environment but have the potential to cause adverse effects on ecology and human health.



According to the database of the Network of Laboratories, Research Centers, and related organizations for monitoring emerging environmental substances (NORMAN network), over 700 compounds of emerging concern have been identified. These compounds are classified into different categories depending on their use and origin:

- i) Persistent Organic Pollutants (POPs).
- ii) Pharmaceuticals and Personal Care Products (PPCPs).
- iii) Endocrine-Disrupting Chemicals (EDCs).
- iv) Agricultural chemicals (herbicides, pesticides).

These contaminants enter the environment through various pathways, such as hospitals, industrial facilities, and households. Subsequently, they are transported to wastewater treatment plants and continuously released into surface and groundwater systems. This is because wastewater treatment plants are not designed to remove these contaminants due to their low concentrations, wide variety and different physical properties that pose when are present in water (Lin et al., 2020; Parida et al., 2021; Riva et al., 2019; Taheran et al., 2018).

The presence of ECs has been detected in surface water systems (rivers and lakes), groundwater, drinking water, wastewater, and effluents from wastewater treatment plants, with concentrations ranging from nanograms per liter (ng/L) to micrograms per liter (µg/L) (Chaturvedi et al., 2021; López-Pacheco et al., 2019; Sharma et al., 2019). They have been found in areas where they have never used, as some ECs are persistent and bio accumulative.

The lack of information on the origin, behavior, impact, and risks of ECs in the environment poses a significant challenge for governments worldwide in terms of controlling and regulating these contaminants. Currently, there are no laws establishing maximum concentrations of ECs in surface and groundwater, drinking water, and the environment. However, some countries have implemented strategies to observe, identify, control and monitor the presence of ECs. For example, the European Union has established different directives and regulations for the control of pesticides (Regulation (EC) No. 1107/2009), pharmaceuticals (Directive 2001/82/EC), and

industrial chemicals (Regulation (EC) No. 1907/2006). It has also listed 45 priority compounds and set environmental quality standards for water systems, in addition to adding another 10 to the contemporary monitoring list (Decision (EU) 2015/495).

In recent decades, advances in environmental ecotoxicology have shown that, even at low concentrations in water sources, ECs pose a potential risk to ecosystem integrity. ECs have been reported to cause sexual disorders in marine organisms (Azizi-Lalabadi and Pirsheh, 2021), neurological, reproductive, and immunological disturbances in animals (Furian et al., 2022), cancer (Lei et al., 2015), the development of antibiotic-resistant bacterial genes (Chaturvedi et al., 2021), congenital heart disease (Gorini et al., 2014), among other toxic effects. However, precise information on the toxic effects of ECs in water systems remains limited and is linked to the complex physicochemical characteristics of ECs, resulting in unpredictable behaviors when present in the environment (Gogoi et al., 2018; Wilkinson et al., 2017).

The United Nations General Assembly adopted the 2030 Agenda for Sustainable Development, recognizing the importance of preventing, controlling, and managing ECs to protect marine biodiversity (Goal No. 14), terrestrial life (Goal No. 15), water quality (Goal No. 6), and to promote responsible consumption and sustainable production (Goal No. 12).

### **2.3 Contamination by pharmaceutical compounds**

Currently, a category of ECs that has gained priority is that of pharmaceuticals (Ahuja, 2021). Pharmaceuticals are widely used in the diagnosis, treatment, cure, and prevention of various diseases in humans and animals, owing to their diverse physicochemical and biological properties. These drugs encompass a wide range of substances, including non-steroidal anti-inflammatory drugs, antihistamines, antibiotics, antiepileptics,  $\beta$ -blockers, and more.

Most pharmaceutical compounds undergo transformations in the body when ingested, leading to the release of a large number of metabolites into surface and groundwater systems (Bexfield et al., 2019; Zhou et al., 2019). These metabolites may undergo additional transformations during wastewater treatment (Ramírez-Morales et

al., 2020). Moreover, they can be degraded by photolysis or hydrolysis, generating degradation by-products with similar or even higher toxicity than the original compounds, posing a risk to humans and ecosystems (Hossain et al., 2018; Nantaba et al., 2020; Serwecińska, 2020). Therefore, reducing the concentrations of pharmaceutical compounds in water systems is of paramount importance.

Although information on the potential toxic effects caused by the presence of pharmaceutical compounds in water is still limited, studies have reported that water contamination with these compounds can lead to the development of antibiotic-resistant bacterial genes (Amarasiri et al., 2020), genotoxic effects (Phong Vo et al., 2019), hormonal disorders (Schaefer and Zito, 2023), and disruptions in the reproduction, growth, and mortality of aquatic organisms (Nkoom et al., 2019).

### **2.3.1 Antihistamines**

Antihistamines are widely used medications for treating allergic diseases. However, their applications have also been discovered in the treatment of inflammatory, autoimmune, and neurological disorders (Pearlman, 1976). Since their introduction to the market in the 1940s, more than 45 classes of antihistamines have been developed, including notable ones such as chlorpheniramine, ranitidine, cetirizine, loratadine, and diphenhydramine. Unfortunately, their presence has been frequently observed in various water bodies worldwide (Kristofco and Brooks, 2017). For instance, Guruge et al. (2019) found chlorpheniramine in surface waters in Sri Lanka, with concentrations of 1.36 ng/L. Other studies reported the presence of chlorpheniramine in the effluent of a wastewater treatment plant in Australia, with concentrations of 4.9 ng/L (Roberts et al., 2016). The presence of antihistamines in water has proven to be a serious environmental risk, especially for aquatic life (Berninger et al., 2011; Isidori et al., 2009; Schaefer and Zito, 2023; Teixeira et al., 2017). One study found that chlorpheniramine induces hormonal disruptions and other negative effects, such as central nervous system depression and dangerous hyperpyrexia (Schaefer and Zito, 2023). Moreover, most antihistamines in water have been found to have the ability to generate toxic by-products, such as nitrosamines,

particularly N-nitrosodimethylamine (NDMA). This substance forms during disinfection/oxidation treatment in wastewater treatment plants (Lv et al., 2015; White and Hernandez, 2021) and has been classified as a Category B2 carcinogenic compound by the United States Environmental Protection Agency (USEPA).

### **2.3.2 Antibiotics**

Antibiotics constitute a class of drugs with a significant impact on the quality of water systems. Due to their potent ability to inhibit and eliminate bacterial growth, these substances are widely used to treat infectious diseases in both humans and animals. Global antibiotic consumption is estimated to range between 100,000 and 200,000 tons annually (Milić et al., 2013; Ngigi et al., 2020). Some commonly used antibiotics include trimethoprim, sulfamethoxazole, tetracycline, metronidazole, ronidazole, and ciprofloxacin.

Most antibiotics exhibit low absorption in the human body, meaning that approximately 80 % of the antibiotic is released in its active form or as a metabolite into water systems. These substances are transported through sewer networks and discharged into surface and groundwater systems. Antibiotic concentrations in various water bodies worldwide have been shown to exceed safe levels by up to 300 times (Vasilachi et al., 2021). For instance, concentrations of trimethoprim in surface water have been detected ranging from 0.5 to 27.43 ng/L (Chernova et al., 2021; Letsinger et al., 2019; Zhang et al., 2018), and in effluents from wastewater treatment plants, concentrations range from 33 to 788 ng/L (Biel-Maeso et al., 2018; Chernova et al., 2021). On the other hand, tetracycline has been found in different water bodies at concentrations ranging from 0.11 to 1300 µg/L (Chernova et al., 2021; Gao et al., 2012; Lin et al., 2009; Zhang et al., 2018). Hospital waste also represents a significant source of water pollution (Halling-Sørensen, 2000; Jjemba, 2006; Lofrano et al., 2020).

The presence of antibiotics in water can lead to mutagenic reactions, giving rise to new antibiotic-resistant bacterial genes. These genes can spread to other bacterial strains, affecting the growth and reproduction of aquatic species (Brain et al., 2004; Lützhøft et al., 1999; Yilmaz and Özcengiz, 2017). Additionally, antibiotics can inhibit

crop growth (Farkas et al., 2007) and have detrimental effects on human health (Amarasiri et al., 2020), rendering them potentially hazardous contaminants.

### **2.3.3 Nonsteroidal anti-inflammatories**

Nonsteroidal anti-inflammatory drugs (NSAIDs) are a common group of medications used to treat inflammations and musculoskeletal pain, such as rheumatoid arthritis, fever, headaches, colds, toothaches, etc. In recent years, they have also been frequently used to treat infections caused by Covid-19 (Micallef et al., 2020; Wojcieszynska et al., 2022). Due to their low cost, accessibility, and availability as over-the-counter medications, NSAIDs are widely consumed globally, raising concerns about river and lake pollution (Madikizela and Ncube, 2021; Rastogi et al., 2021).

Currently, there are more than 100 NSAID compounds, with ibuprofen, naproxen, diclofenac, and acetaminophen being prominent among them. These compounds are released from various pollution sources and are found in significant concentrations in surface water and the effluents of wastewater treatment plants. For example, diclofenac has been detected in surface water at concentrations ranging from 1.0 to 51.4 ng/L, while acetaminophen at concentrations of 31.5 to 902 ng/L (Chernova et al., 2021; Kondor et al., 2020; Letsinger et al., 2019; Zhang et al., 2018). Furthermore, diclofenac and acetaminophen have been located in effluents from wastewater treatment plants at concentrations of 38 to 1020 ng/L and 17 to 441 ng/L, respectively (Biel-Maeso et al., 2018; Chernova et al., 2021).

While the presence of NSAIDs in water bodies is widely acknowledged, information on their ecotoxicological risk is still limited. A study by Sathishkumar et al. (2020) revealed that diclofenac causes adverse effects on the reproduction of griffon vultures, as well as cardiotoxic, hepatotoxic, nephrotoxic, neurotoxic, genotoxic, and hematotoxic effects in mammals. It has also been observed to affect the liver, kidneys, and gills of fish, as well as cytotoxicity and genotoxicity in plants, and a decrease in the survival and reproduction of invertebrate organisms. On the other hand, acetaminophen has been found to alter the genetic code and cellular function in both

humans and aquatic animals, depending on the level of exposure to the contaminant (Phong Vo et al., 2019).

#### **2.3.4 Antiepileptics**

Epilepsy is one of the most common neurological disorders, characterized by frequent seizures, loss of consciousness, and gastrointestinal dysfunction (Kwan and Brodie, 2001). According to the World Health Organization (WHO), over 50 million people worldwide are affected by epilepsy. Antiepileptic medications are used to treat seizures associated with epilepsy, but they are also employed for other conditions such as migraines, chronic neuropathic pain, and mood disorders, leading to a significant increase in their consumption in recent years (Carmland et al., 2022; Ho et al., 2021; Parikh and Silberstein, 2019).

Carbamazepine, gabapentin, lamotrigine, and primidone are the antiepileptics most frequently detected and found in elevated concentrations in rivers and lakes worldwide (Anim et al., 2020; Challis et al., 2018; Ebele et al., 2020; Kondor et al., 2020; Park and Lee, 2018; Sanz-Prat et al., 2020; White et al., 2019). In a study, Kondor et al. (2020) reported high concentrations of carbamazepine in the Danube River, with value of 47.6 ng/L. Generally, carbamazepine has been detected in various water bodies at concentrations ranging from 3.0 to 72.01 ng/L (Chernova et al., 2021; Zhang et al., 2018). Additionally, it has been found in effluents from wastewater treatment plants at concentrations of 21 to 657 ng/L (Biel-Maeso et al., 2018; Chernova et al., 2021).

Antiepileptics, especially carbamazepine, are contaminants that rise significant environmental concerns due to their toxic effects on aquatic ecosystems. Numerous studies have been reported that carbamazepine has severe effects on aquatic organisms, including impacts on the reproduction rate, growth, and mortality of planktonic crustaceans, algae, and invertebrates (Nkoom et al., 2019; Zhang et al., 2012; Zind et al., 2021). Additionally, genetic alterations and acute toxic effects have been observed in rainbow trout exposed to this compound (Li et al., 2010, 2011), increased mortality of zebrafish embryos and larvae (da Silva Santos et al., 2018; Pohl

et al., 2019), as well as morphological changes in cnidarians (Quinn et al., 2009). On the other hand, little research has been conducted on the toxic effects of antiepileptics on human health. Some authors have examined the effects of carbamazepine on human health when present in water, and although it is concluded that carbamazepine does not pose a potential risk to human health, continued monitoring of its behavior is necessary due to the adverse effects it may have when consumed for medical purposes (Cunningham et al., 2010; Houeto et al., 2012). For example, Abuzneid et al. (2022) reported that the ingestion of carbamazepine by 23-year-old patient led to the development of Stevens-Johnson syndrome and toxic epidermal necrolysis, which are skin reactions causing high fever and ulcers in the mouth and face. Additionally, carbamazepine has been found to cause congenital malformations when consumed during pregnancy (Andrade, 2018; Jentink et al., 2010; Jones et al., 1989; Sutcliffe et al., 1998).

## **2.4 Methods for the removal of pharmaceutical compounds from water solutions**

Currently, wastewater treatment plants play a crucial role in eliminating various contaminants, such as suspended particles, dissolved organic compounds, nutrients, and pathogens. These plants employ different treatment stages involving processes like screening, coagulation/flocculation, centrifugation, sedimentation, and biological treatments. However, current conventional technologies have limitations in reducing concentrations of pharmaceutical compounds in wastewater (Rout et al., 2021). To address this challenge, there has been ongoing work in the development and implementation of more effective and specific treatment technologies. Notable among these technologies are methods such as chlorination, ozonation, adsorption, advanced oxidation processes, and visible light photodegradation (Ahmed et al., 2021; Kavitha, 2022; Krakkó et al., 2022; Liu et al., 2019; Obradović et al., 2022; Wang et al., 2023). These innovative technologies have shown promise in the removal of pharmaceutical compounds and other persistent contaminants in wastewater, undergoing continuous research and development.

Ozonation relies on ozone as strong oxidizing and disinfecting agent to degrade organic contaminants. Recently, catalytic and photocatalytic ozonation techniques have been proposed to enhance the formation of hydroxyl radicals, favoring the degradation and mineralization of pharmaceutical compounds (Issaka et al., 2022). A study by Li et al. (2022) investigated the degradation of trimethoprim through catalytic ozonation using a ceramic membrane functionalized with manganese-iron binary oxides (Mn/FeOx). The results showed a 98.6 % removal of trimethoprim. However, the study also detected the formation of hard-to-mineralize intermediate products, achieving only around 50 % mineralization of trimethoprim.

Chlorination involves the use of free chlorine and chlorine dioxide (ClO<sub>2</sub>) to degrade active organic compounds (Crain and Gottlieb, 1935). In a recent study, simultaneous or multicomponent chlorination of sulfamethoxazole, acetaminophen, and diclofenac in acidic, neutral, and alkaline solutions was investigated. The study revealed that degradation capacity depended on the solution pH, decreasing in the order of sulfamethoxazole > diclofenac > acetaminophen in acidic solution, sulfamethoxazole > acetaminophen > diclofenac in alkaline solution. Additionally, the study discovered the formation of unknown dimers, sulfamethoxazole-acetaminophen and sulfamethoxazole-diclofenac, as degradation byproducts during simultaneous chlorination (Liu et al., 2019). These findings highlight the complexity of chlorination processes and their effects on the formation of undesirable byproducts, which may have significant implications for the safety and effectiveness of pharmaceutical compound removal through this method.

Visible light photodegradation is an emerging technology for water treatment capable of completely breaking down organic contaminants in aqueous solutions. In this process, an oxidant is used to break down pharmaceutical compounds into short-chain organic acids, inorganic acids, and CO<sub>2</sub>, generating hydroxyl radicals (Kavitha, 2022). A study by Guo et al. (2021) evaluated the photocatalytic activity of tubular hollow graphene carbon nitride decorated with copper phosphide nanoparticles (Cu<sub>3</sub>P/HTCN) in the visible light photodegradation of tetracycline. The results demonstrated that Cu<sub>3</sub>P/HTCN exhibited high photocatalytic efficiency in tetracycline



degradation, achieving a 96.9 % efficiency in just 40 minutes. Despite the advantages of visible light photodegradation in removing pharmaceutical compounds from water (Kutuzova et al., 2021; Li et al., 2019; Xu et al., 2021), this technology still faces challenges requiring thorough study before large-scale implementation. These challenges include the cost of photocatalysts, chemical stability, infrastructure needed for identification and analysis of degradation byproducts, large-scale reactor design, and environmental efficacy. These factors limit its implementation compared to other water treatment technologies.

Advanced Oxidation Processes (AOPs) are innovative and highly effective strategies for wastewater treatment. These processes accelerate the degradation rate of organic contaminants and promote mineralization by generating intense hydroxyl radicals (Glaze et al., 1987; Klavarioti et al., 2009; Legrini et al., 1993; Malato et al., 2009). Examples of AOPs for the oxidation of organic contaminants include photocatalysis using titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) (Panwar et al., 2022), solar-assisted electrooxidation (Ding et al., 2021), ozone-based electrochemical processes (Bavasso et al., 2022), hydrogen peroxide (Wang et al., 2023), UV chlorination photolysis (Guo et al., 2022), and Fenton processes (Dargahi et al., 2021). Numerous studies have been conducted on the use of these advanced oxidation processes for the removal of pharmaceutical compounds from aqueous solutions. For instance, Nguyen et al. (2022) investigated the degradation of antibiotics cephalexin and tetracycline using novel Ni-doped TiO<sub>2</sub>-based photocatalysts. The results showed that the photocatalytic degradation of cephalexin and tetracycline reached 91.6 % and 82.5 %, respectively, and after 5 reuse cycles, the degradation capacity remained above 75 %. In another study, the degradation of acetaminophen by ultrasound-assisted electro-Fenton using iron oxide nanoparticles as a catalyst (HNPs) was reported. The photocatalytic activity of HNPs was found to be superior to other photocatalysts prepared with different transition metals. For example, at an initial concentration of 20 mg/L of acetaminophen, degradation reached 98.9 %, decreasing by at least 14 % after the fourth reuse cycle (Ghanbari et al., 2021). Despite the high degradation capacity of pharmaceutical compounds demonstrated by advanced

oxidation processes (AOPs), concerns arise due to the formation of degradation byproducts that may be more toxic than the original pharmaceutical. Liu et al. (2016) identified the presence of at least 31 degradation byproducts of oxytetracycline, generated through reaction mechanisms including hydroxylation, secondary alcohol oxidation, demethylation, decarbonylation, and dehydration. This raises issues about the potential environmental impact of these toxic byproducts. Additionally, AOPs face limitations in water with high organic content and turbidity, which hinders the penetration of UV radiation (Homem and Santos, 2011). Furthermore, the high consumption of chemicals in AOPs can lead to significant secondary contamination concerns and increased treatment costs in the medium term (Martínez-Huitle and Ferro, 2006).

Adsorption processes emerge as a highly promising and effective alternative for the removal of pharmaceuticals from wastewater. This technology presents several advantages, making it an appealing choice when compared to other treatment techniques. Noteworthy features include ease of operation, cost-effectiveness, reproducibility, high efficiency, and the absence of toxic byproduct generation (Sophia A. and Lima, 2018). Moreover, it offers flexibility in utilizing a broad range of adsorbent materials, ranging from natural micrometric substances to advanced nanostructured synthetic materials (Carrales-Alvarado et al., 2020; García-Reyes et al., 2021; Maggio et al., 2022; Moral-Rodriguez et al., 2020; Ortiz-Ramos et al., 2022).

#### **2.4.1 Adsorption**

Adsorption is a surface process involving the accumulation of a substance, called the solute, on the surface of a typically porous solid. The substance adhering to the solid is known as the adsorbate and can be an ion or a molecule, while the solid where adsorption occurs is termed the adsorbent (Cooney, 1998).

Adsorption of the adsorbate onto the surface of the adsorbent can occur due to physical or chemical interactions and is classified as either physical adsorption or chemical adsorption. Physical adsorption arises from molecular interactions between the solid surface and the adsorbate molecules. These interactions can be electrostatic,

van der Waals forces, hydrogen bonding, or London dispersion forces. Due to these weak interactions, the adsorbate can move freely on the surface, rendering the adsorption reversible. In contrast, chemical adsorption involves a strong chemical interaction between specific active sites on the adsorbent and adsorbate molecules. In this case, the chemical interaction typically involves the formation of chemical bonds, resulting in irreversible adsorption. Additionally, the heat of adsorption in chemical adsorption is high, exceeding 40 kJ/mol, similar to that of chemical reaction (Leyva-Ramos, 2010).

Liquid-phase adsorption is influenced by various factors affecting interactions between the adsorbate and the adsorbent, including:

- i) *Morphology and textural properties of the adsorbent:* The adsorption capacity depends on the textural and morphological properties of the adsorbent, such as specific surface area, pore volume and diameter, and pore size distribution. These properties impact the availability and accessibility of the area where adsorption occurs.
- ii) *Surface charge and zero-point charge.* The adsorbent in an aqueous solution can acquire a charge on its surface, which can be positive, neutral, or negative, depending on the solution pH. Studying the distribution of surface charge and the zero-point charge of the adsorbent is crucial for understanding adsorption mechanisms.
- iii) *Concentration and type of active sites.* The adsorbent material has functional groups on its surface that can donate or accept protons depending on the solution pH. Proton-donating sites are acidic, while proton-accepting sites are basic. The concentration and type of active sites are fundamental characteristics for adsorbing cations or anions.
- iv) *Nature of the adsorbate.* The adsorption capacity is strongly influenced by the physicochemical properties of the adsorbate, such as concentration, molecular size, polarity, solubility, composition, and chemical speciation.
- v) *Liquid phase characteristics.* Properties of the liquid phase, such as pH, temperature, ionic strength, and solvent type, affect the adsorption capacity. In

particular, the pH of the solution plays a crucial role since the surface charge of the adsorbent depends on the pH. Furthermore, for compounds that ionize in aqueous solution by donating or accepting protons, the adsorption capacity varies considerably with pH.

- vi) *Presence of other substances.* The presence of additional contaminants can harm, not affect, or enhance the adsorption capacity of the organic compound under study. When an additional adsorbate hinders the adsorption of the target adsorbate, a competitive or antagonistic effect occurs. Conversely, when the presence of another adsorbate promotes adsorption capacity, a cooperative or synergistic effect takes place. Finally, when the adsorption capacity is unaffected by the presence of another adsorbate, the multicomponent adsorption system is said to have a non-interactive effect.

## **2.5 Adsorbent materials**

Activated carbon stand out as the primary adsorbent material widely used in industrial wastewater treatment (Perrich, 1981). However, ongoing research is exploring numerous natural and synthetic adsorbent materials for the removal of pharmaceutical contaminants from aqueous solutions. These materials include natural soils (Rodríguez-López et al., 2022), natural clays (Ortiz-Ramos et al., 2022), organoclays with Gemini surfactants (Guo et al., 2019), magnetic biocarbonized materials (Dai et al., 2020), magnetite-doped graphene oxides (Lin et al., 2019), metal-organic frameworks (Cheng et al., 2022), molecularly imprinted polymers (Cantarella et al., 2019), carbon xerogels (Moral-Rodriguez et al., 2020), and carbon nanotubes (Carrales-Alvarado et al., 2020).

In general, the activity and capacity of an adsorbent material depend on its physicochemical properties, influenced by the nature of the raw material, the separation process, and the synthesis parameters used. There are certain key characteristics that an adsorbent material should possess:

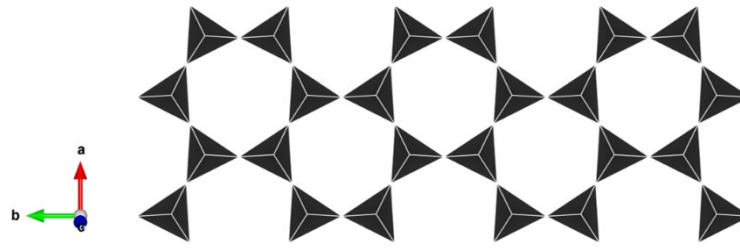
- i) Low cost and abundant availability.
- ii) Ease of synthesis and manipulation.

- iii) Chemical, thermal and mechanical stability.
- iv) Appropriate chemical, texture, and particle size properties.
- v) High adsorption capacity and rate.
- vi) Easy regeneration and reusability.

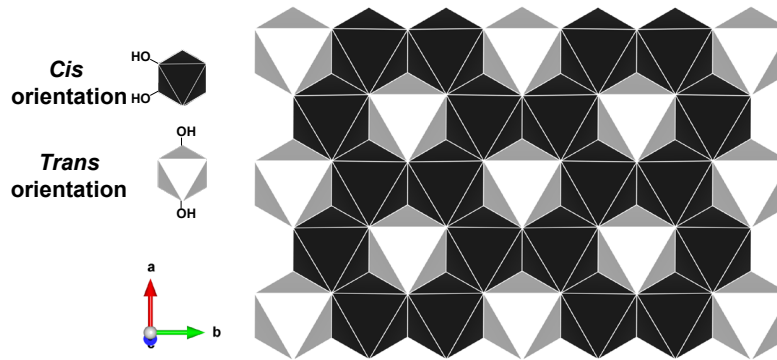
### 2.5.1 Natural clays

Clays are a category of hydrated phyllosilicates that constitute a significant portion of the fine-grained fraction found in rocks, sediments, and soils. These natural materials are predominantly composed of silicon, aluminum, oxygen, and hydrogen (Domínguez and Schifter, 1992). They are characterized by negative surface charges and a colloidal structure, providing them with chemical stability and expansive capacity. These properties enable clays to retain and trap metallic cations and certain organic compounds on their surface (Chaari et al., 2019; Padilla-Ortega et al., 2013).

The structure of clays is marked by an organized arrangement of tetrahedral (T) and octahedral (O) layers. Each layer consists of tetrahedra formed by a cation coordinated with four oxygen atoms. These tetrahedra are connected through three shared corners with adjacent tetrahedra, creating a two-dimensional hexagonal lattice pattern along the crystallographic directions a and b (T-layer). The tetrahedron contains a silicon ( $\text{SiO}_4$ )<sup>4-</sup> or aluminum ( $\text{AlO}_4$ )<sup>5-</sup> atom at its center (Figure 2.1). On the other hand, the octahedral layer is composed of octahedra formed by a cation coordinated with six oxygen and hydroxyl atoms. These octahedra are connected sharing oxygens and hydroxyls at the edges of one octahedron with those at the edges of another octahedron. The octahedra exhibit two different topologies based on the position of the hydroxyl group, cis and trans. As a result, the octahedral layer can display a hexagonal or pseudohexagonal structure (O-layer) (Figure 2.2). The central cation in each octahedron can be aluminum, iron, or magnesium, resulting in the following chemical composition:  $[(\text{Al/Fe})\text{O}_n (\text{OH})_m]^-$  or  $[(\text{Mg/Fe})\text{O}_n (\text{OH})_m]^-$ . In these formulas,  $n + m = 6$  (Brigatti et al., 2013).



**Figure 2.1.** Tetrahedral sheet of clays.



**Figure 2.2.** Octahedral sheet of clays.

The T and O sheets in clays can join through the oxygen atoms at the vertices of the tetrahedra and octahedra, forming a planar arrangement of laminar structures. The combination of one T sheet with the one O sheet results in T:O or 1:1 lamellar block, known as bilaminar structures. Alternatively, two T sheets can join with one O sheet to form T:O:T or 2:1 trilaminar structures. The clay structure can be dioctahedral or trioctahedral, depending on how the octahedral and tetrahedral sheets are joined. In a dioctahedral structure, two-thirds of the octahedral sites are occupied by trivalent atoms such as  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . In trioctahedral sheets, all octahedral sites are occupied by divalent atoms such as  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  (Velde, 1992).

The formed lamellar blocks can be electrically neutral or negatively charged. Electrical neutrality occurs when: i) the octahedral sheet contains trivalent cations ( $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ ) in two octahedral sites and a vacancy in the third octahedron; ii) all octahedral sites are occupied by divalent cations ( $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$ ); and iii) the tetrahedral sheet contains  $\text{Si}^{4+}$  in all tetrahedral sites. On the other hand, the negative charge in clays is

due to i) the substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  in tetrahedral sites; ii) the substitution of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  by lower charged cations in octahedral sites, usually  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$ ; and iii) the presence of vacancies. These substitutions are known as isomorphic substitutions, as they do not alter the morphology of the lamellar block (Brigatti et al., 2013).

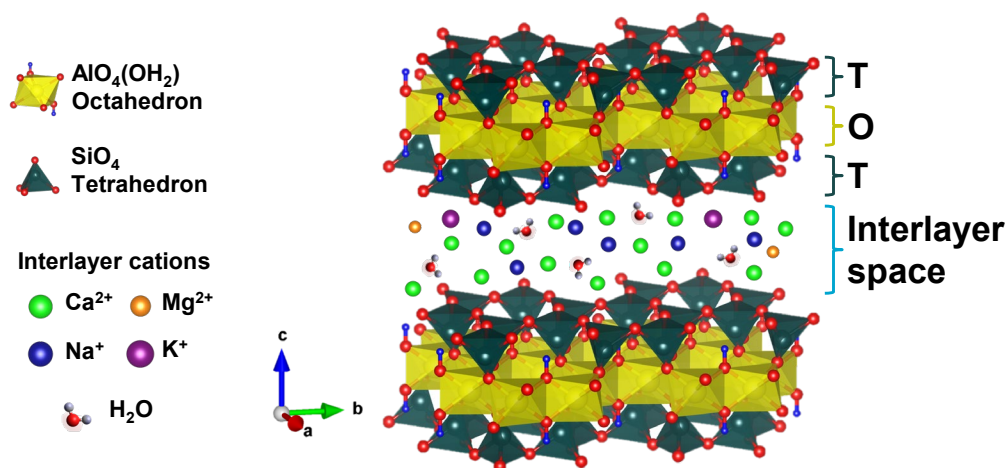
Clays, especially those with a 2:1 layered structure such as smectites, vermiculites, and micas, are characterized by their charge variability, enabling the occupation of spaces between each laminar block by exchangeable cations. In addition to this characteristic, clays possess other distinctive properties:

- i) Laminar structure on a nanometric scale: Bilaminar blocks 1:1 (T:O) have an approximate thickness of 0.7 nm, while trilaminar blocks 2:1 (T:O:T) have a thickness close to 1 nm (Moore and Hower, 1986).
- ii) Capacity to exchange cations.
- iii) Hydration, plasticity, and swelling.
- iv) Different types of surfaces: external surface, edge surfaces, and interlayer space surface.
- v) Surface modification: Clay surfaces are easily modifiable, allowing the creation of hybrid materials with additional functionalities.

Bentonite is a natural clay primarily found in the form of montmorillonite and belongs to the smectite group (Figure 2.3). Its 2:1 layered structure comprises an octahedral sheet, primarily containing trivalent  $\text{Al}^{3+}$  cations (dioctahedral structure), situated between two tetrahedral sheets of  $\text{Si}^{4+}$ . Isomorphous substitutions of cations in the sheets generate an excess of negative charge, balanced by exchangeable and hydratable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  present in the interlayer space, forming weak bonds. Hydration of interlayer cations can occur in two ways: inner-sphere hydration and outer-sphere hydration. In inner-sphere hydration, the cation interacts with the clay surface on one side and with water molecules on the other side. In contrast, in outer-sphere hydration, the cation is fully surrounded by water molecules interacting with the clay surface through hydration water.

The capacity of bentonite to adsorb cations is attributed to its Cation Exchange Capacity (CEC), expressed in units of centimoles of positive charge per kilogram of

clay (cmol(+)/kg). CEC exhibits the following characteristics: i) it is reversible; ii) it is stoichiometric; and iii) it shows selectivity of one cation over another.



**Figure 2.3.** Trilaminar structure 2:1 (T:O:T) of a bentonite clay.

Concerning the removal of pharmaceutical compounds by adsorption on natural clays, there is a lack of significant studies in this area. Most research has concluded that natural clays do not exhibit a high adsorption capacity for pharmaceutical compounds. For instance, Thiebault and Boussafir (2019) studied the adsorption of diazepam on montmorillonite and found a low adsorption capacity of 10.2 mg/g at pH = 7.5. In another recent study, Vallova et al. (2022) investigated the ability of montmorillonite to adsorb the analgesics paracetamol, diclofenac, and ibuprofen. The results showed that the clay failed to completely remove the analgesics from the aqueous solution, obtaining adsorption capacities of 3.9, 18.0 and 15 mg/g for paracetamol, diclofenac, and ibuprofen, respectively. These studies conclude that the negative and hydrophilic surface of natural bentonite inhibits the adsorption capacity of pharmaceutical compounds. However, it is important to note that previous research has demonstrated that bentonite can adsorb tetracycline through electrostatic attraction, cation exchange, and complexation, achieving a high adsorption capacity of 283.5 mg/g at pH = 3 (Ortiz-Ramos et al., 2022). Similar results were obtained in a study by Wu et



al. (2019), where the adsorption of the antibiotic ciprofloxacin on montmorillonite was investigated.

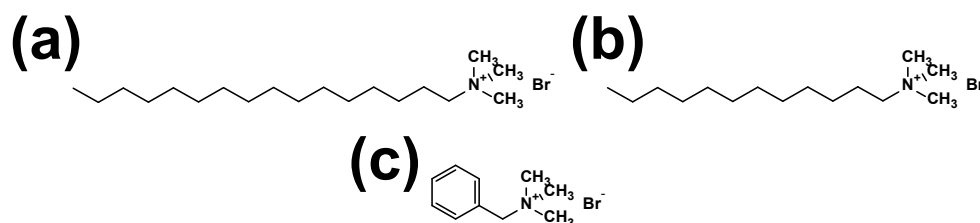
These findings suggest that, although natural clays generally have limitations in the adsorption of pharmaceutical compounds, specific mechanisms and particular conditions can influence their adsorption capacity. Further research is needed to understand and optimize the adsorption capacity of natural clays for pharmaceutical compounds, as well as to explore possible surface modifications that may enhance their effectiveness in removing these compounds.

### **2.5.2 Organoclays**

Organoclays are highly innovative and of great interest, obtained by modifying natural clays with organic compounds. This surface modification provides them with new functionalities, making them applicable in various fields such as rheological control agents, paints, cosmetics, refractory varnishes, and thixotropic fluids (de Paiva et al., 2008). In recent years, organoclays have been found to exhibit a remarkable adsorption capacity for organic molecules in aqueous solutions (Martín et al., 2019; Martinez-Costa et al., 2018; Shah et al., 2018; Shen and Gao, 2019; Tariq et al., 2022). This discovery has opened up new opportunities for their application in the removal of pharmaceutical contaminants from wastewater.

The synthesis of organoclays is based on reactions involving clays and organic compounds and can occur through two different reaction routes: i) solid-state reactions and ii) cation exchange reactions. In the first case, organic molecules can be intercalated into dry clay without the use of solvents, thanks to ion-dipole interactions, where the polar groups of the organic compound interact with the interlayer cations (Garikoé and Guel, 2022; Lagaly et al., 2013). In the second case, interlayer cations are exchanged for cationic surfactants, such as quaternary ammonium salts, in an aqueous solution (Leyva-Ramos et al., 2021). Additionally, in some cases, other types of organic compounds such as Gemini surfactants (Shen and Gao, 2019), amino acids (Imanipoor et al., 2021), phospholipids (Liu et al., 2017), and even polymeric macromolecules (Kausar et al., 2019) can be used to achieve clay modification.

Cation exchange reactions with cationic surfactants enable the preparation of organoclays, modifying the surface nature of the clay from hydrophilic to hydrophobic and organophilic, simultaneously generating positively charged anionic sites on its surface. Cationic surfactants consist of a quaternary ammonium group attached to an organophilic chain and are represented by the general formula  $(\text{CH}_3)_3\text{NR}^+$ , where R can be an alkyl chain or a benzyl group. Among the most commonly used surfactants for organoclay preparation are hexadecyltrimethylammonium bromide (HDTMA), dodecyltrimethylammonium bromide (DDTMA), and benzyltrimethylammonium bromide (BTMA) (Leyva-Ramos et al., 2021; Martinez-Costa and Leyva-Ramos, 2017). Their chemical structures are illustrated in Figure 2.4.

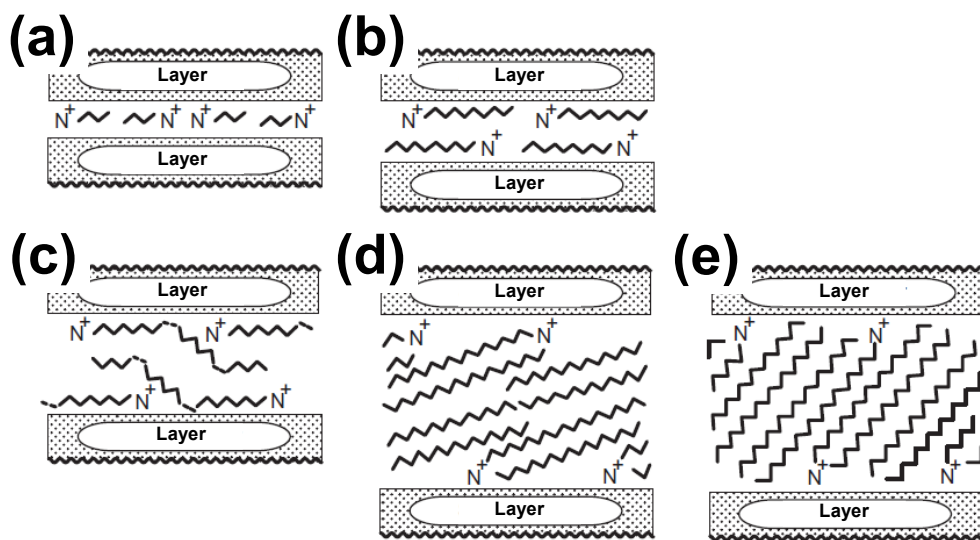


**Figure 2.4.** Chemical structures of the cationic surfactants HDTMA (a), DDTMA (b) and BTMA (c).

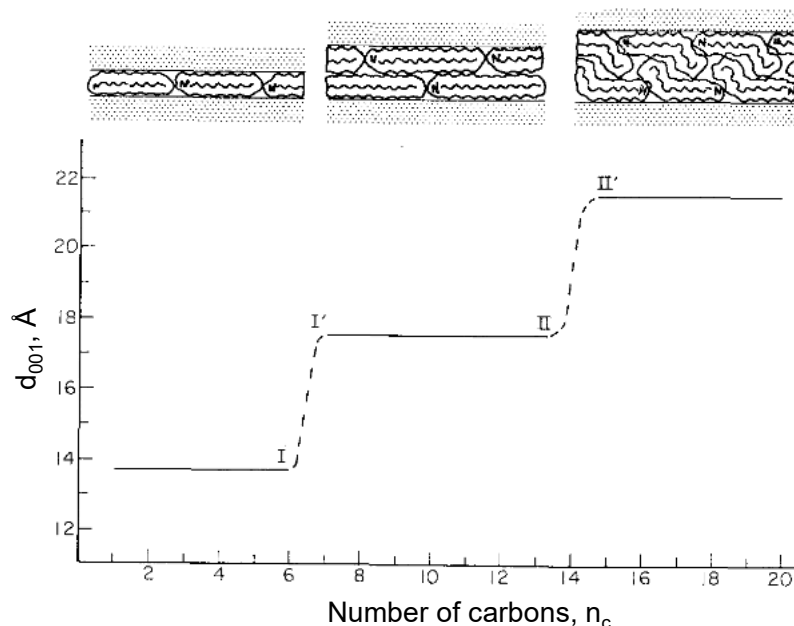
The structural arrangement of organoclays is primarily determined by the packing density of interlayer cations and the length of the alkyl chain of the cationic surfactant. However, other factors such as surface geometry and the cation exchange capacity of the clay can also influence this structure. As a result, organoclays can adopt various structural configurations, including monolayers, bilayers, pseudotrimolecular layers, and paraffin-like structures. Figure 2.5 illustrates some of these structural configurations (Lagaly et al., 2013).

The structural configuration of organoclays can be determined by measuring the basal spacing ( $d_{001}$ ) of the organoclay, which is influenced by the length of the cationic surfactant chain, as shown in Figure 2.6. According to Lagaly et al. (2013), a monolayer arrangement will form when the alkylammonium chains are short ( $n_c < 6$ ), while a bilayer will form when the alkylammonium chains are long ( $n_c > 7$ ). In both cases, the

alkylammonium chains are arranged parallel to the clay layers. The  $d_{001}$  distance in a monolayer is generally 1.35 nm, and the interaction occurs at the negatively charged cationic sites of the clay layers, attributed to electrostatic attraction and cation exchange. The bilayer has a  $d_{001}$  value of 1.77 nm and interacts with the previously adsorbed monolayer through van der Waals interactions between the alkyl chains of the cationic surfactant (Leyva-Ramos et al., 2021). As the length of the alkyl chain increases ( $n_c > 14$ ), a transition to a pseudotrimolecular structural configuration occurs, along with an increase in the  $d_{001}$  value. In this case, the positive group  $(CH_3)_3N^+$  is located near to the cationic sites of the clay layer, and the chains arrange in a “twisted” trimolecular arrangement. The pseudotrimolecular structure typically exhibits a  $d_{001}$  value of 2.15 nm. Increasing the length of the alkyl chain and the cationic surfactant/clay ratio has been observed to make organoclays more hydrophobic (Martinez-Costa and Leyva-Ramos, 2017). Finally, the paraffin-like arrangement is found in quaternary ammonium surfactants that contain two or more long alkyl chains, such as phospholipids (Wicklein et al., 2010).



**Figure 2.5.** Structural arrangements of organoclays: monolayer (a), bilayer (b), pseudotrimolecular layer (c) and inclined paraffin-like structures (d, e). (Lagaly et al., 2013).



**Figure 2.6.** Variation of basal space,  $d_{001}$ , with cationic surfactant alkyl chain length,  $n_c$ , due to monolayer, bilayer, and pseudotrimolecular layer formation (Lagaly et al., 2013).

Several studies have investigated the adsorption of pharmaceutical compounds on organoclays, yielding varied results. For instance, De Oliveira et al. (2017) examined the adsorption of diclofenac on organomontmorillonite modified with two different surfactants: benzyldimethyltetradecylammonium bromide (BDTA) and hexadecyltrimethylammonium bromide (HDTMA). They found that the adsorption capacity of diclofenac varied slightly depending on the surfactant used. Materials prepared with BDTA and HDTMA showed diclofenac adsorption capacities of 56.3 and 44.4 mg/g, respectively. However, another study obtained a much higher diclofenac adsorption capacity of 361.3 mg/g on HDTMA-modified bentonite (Martinez-Costa et al., 2018). Both works concluded that adsorption is attributed to electrostatic attraction between the anionic species of diclofenac and the anionic and positively charged sites of organoclays. In another recent investigation, the adsorption of paracetamol on organobentonites modified with different surfactants, both anionic (sodium dodecyl sulfate and dodecyl benzene sulfonic acid) and cationic (dodecyltrimethylammonium

bromide and dodecylpyridinium chloride), was studied. The adsorption capacity was found to depend on the type of ionic surfactant used. The organoclay modified with dodecyltrimethylammonium bromide showed the highest paracetamol adsorption capacity of 32.4 mg/g, while the adsorption capacities decreased in the following order: dodecylpyridinium bromide > sodium dodecyl sulfate > dodecyl benzene sulfonic acid (Çalışkan Salihi et al., 2023). The hydrophobic effect on the surfactant chains in the clay was found to play a significant role.

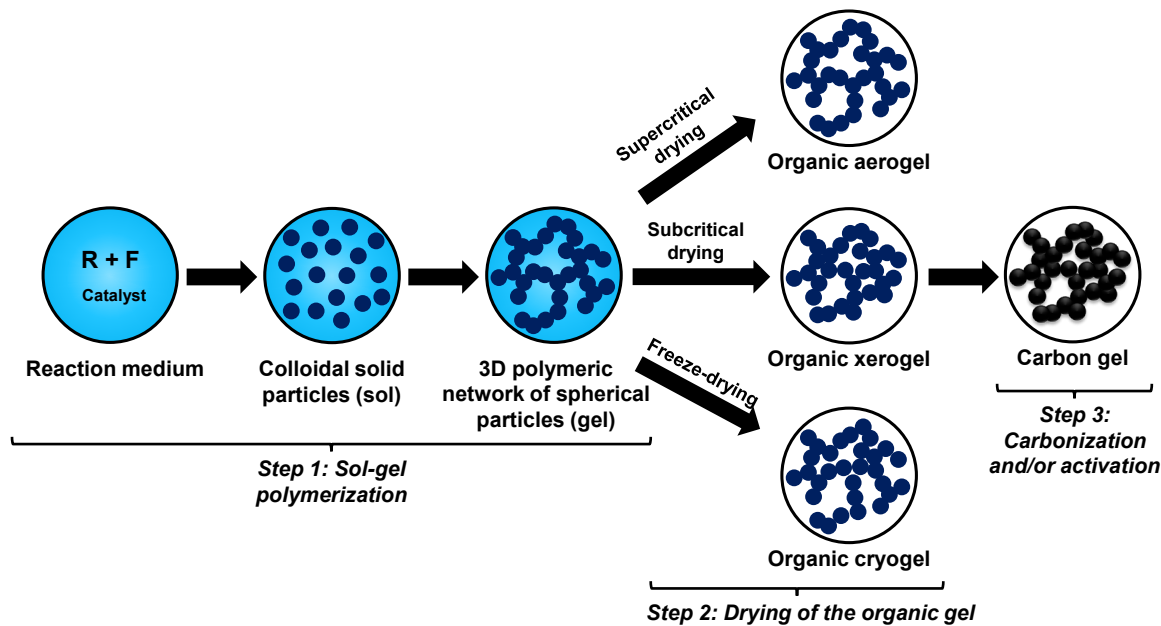
While numerous studies have concluded that organoclays exhibit high adsorption capacities for pharmaceutical compounds (França et al., 2020; Imanipoor et al., 2021; Malvar et al., 2020; Saitoh and Shibayama, 2016; Vallova et al., 2022; Zhang et al., 2021), contradictory results have also been obtained where the organic modification of the clay does not increase or even decreases the adsorption capacity. For example, Yang et al. (2020) analyzed the adsorption of tetracycline on organovermiculite modified with the surfactant dodecyl dimethyl betaine (DDB) and found that the adsorption capacity did not significantly increase with organic modification. At pH = 7, the adsorption capacities were 8.8 and 11.1 mg/g for natural vermiculite and organovermiculite, respectively. Another study investigated the simultaneous adsorption of sulfamethoxazole and trimethoprim on HDTMA-modified organobentonite and found that the organobentonite exhibited high individual adsorption capacity for sulfamethoxazole but not for trimethoprim. The individual adsorption capacities were 55.7 and 8.7 mg/g for sulfamethoxazole and trimethoprim, respectively (Martínez-Costa et al., 2018).

Despite numerous studies on the adsorption of pharmaceutical compounds on organoclays, the reasons why organoclays inhibit or decrease the adsorption capacity for certain pharmaceutical compounds have not been thoroughly investigated. Therefore, further research in this field is crucial to better understand the adsorption mechanisms and optimize the use of organoclays in pharmaceutical compound removal from water.

### 2.5.3 Carbon xerogels

Carbon gels are nanostructured materials with highly controlled chemical composition and porous structure. These materials are formed by the carbonization of an organic gel, commonly synthesized through the sol-gel method (Pekala, 1989). They have found extensive use in various applications (da Cunha et al., 2021; Elmouwahidi et al., 2021; Haye et al., 2020; Prokić et al., 2022; Yang et al., 2020; Zainol et al., 2021). The sol-gel method involves the polymerization of a hydroxylated benzene derivative (such as resorcinol, phenol, cresol, among others) and an aldehyde (such as formaldehyde, furfural, among others) in the presence of a solvent (water, ethanol, methanol, acetone). Once the solvent is removed, the resulting solid organic polymer is called organic gel. Resorcinol, formaldehyde, and water are the most commonly used reagents by various authors (Gaikwad et al., 2019; Ibarra Torres et al., 2021; Job et al., 2005; Li et al., 2019; Lu et al., 2018; Ptazkowska-Koniarz et al., 2018).

The synthesis of carbon gels through sol-gel method consists of three stages (Figure 2.7): i) polymerization, ii) drying of the solvent-saturated gel, and iii) carbonization with or without activation of the gel. In the first stage, resorcinol (R) and formaldehyde (F), dissolved in a reaction medium, undergo addition and condensation polymerization in the presence of a catalyst. The addition and condensation polymerization mechanisms are depicted in Figure 2.8. During this stage, a suspension of colloidal solid particles (sol) forms, which tend to grow and create a three-dimensional polymeric network of interconnected spherical particles (gel) with suitable chemical characteristics and porosity. Synthesis parameters, such as the nature, ratio, and concentration of reagents, catalyst, solvent, and pH of the reaction medium, are crucial for controlling the meso and macroporosity of the gel. The catalyst plays a fundamental role in polymerization, as its nature determines the pH of the reaction medium. Alkali metal carbonates ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{Fr}_2\text{CO}_3$ ) are the most commonly used as catalysts in this method (Alegre et al., 2019; Eckert et al., 2022; Medina et al., 2021; Moral-Rodriguez et al., 2020; Shouman and Fathy, 2018; Yang et al., 2020).



**Figure 2.7.** Stages of synthesis of carbon gels by the sol-gel method (Arenillas et al., 2019).

The drying of the solvent-saturated gel is a crucial stage in synthesis, as it plays a determining role in preserving the porosity of the final organic gel. Capillary forces generated between the solvent and the pore walls can lead to the collapse of the porous structure of the gel. In the literature, three conventional drying methods have been reported: supercritical drying, subcritical drying, and freeze-drying, which differ in the pressure and temperature conditions used to remove the solvent (Gizli et al., 2022; Job et al., 2005). Depending on the drying method employed, the final organic gel may receive different designations. In the case of supercritical drying, an aerogel is obtained, while subcritical drying results in a xerogel, and freeze-drying leads to a cryogel. These designations reflect the specific characteristics of each gel in terms of its porosity and structure.

Supercritical drying is widely employed by various researchers as one of the most common methods. It involves the use of CO<sub>2</sub> under elevated pressure and temperature conditions to remove the solvent (Bakos et al., 2018; Jayaseelan et al., 2018; Li et al., 2019; Liu et al., 2021; Sam et al., 2020; Wang et al., 2022). In the case

where water is the solvent, it is necessary to replace it first with an organic solvent (acetone, methanol, etc.) due to the high solubility of CO<sub>2</sub> in water. During the drying process, CO<sub>2</sub> replaces the organic solvent and is removed in gas form, minimizing capillary forces and preserving much of the original porosity of the gel. The resulting organic gel is known as an aerogel. On the other hand, freeze-drying involves drying the organic gel under cryogenic conditions (Babić et al., 2004; Okay and Lozinsky, 2014). In this case, the solvent is frozen and then removed by sublimation. Similar to supercritical drying, if the solvent is water, it must be exchanged first with an organic solvent to prevent the formation of ice crystals that could significantly impact the porosity of the gel. After solvent removal, the organic gel is referred to as a cryogel. Although these two drying methods are highly effective in preserving the porosity of the final organic gel, they are also expensive and challenging to handle, limiting their application on a large scale.

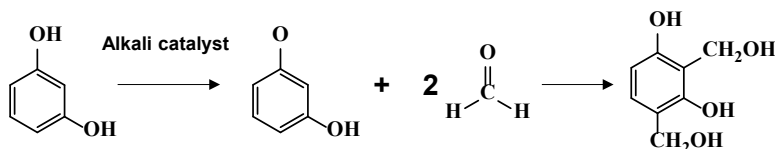
In contrast, subcritical drying is a straightforward and cost-effective method for obtaining organic xerogels on a large scale. It relies on the direct evaporation of the solvent under normal pressure and temperature conditions. Although a liquid-vapor interface forms during the drying process, which can potentially lead to collapse of the gel structure due to surface tension, it has been demonstrated that, under controlled operating conditions, it is possible to minimize such collapse and obtain organic xerogels with very well-controlled porosity (Bailón-García et al., 2020; Castelo-Quibén et al., 2019; Medina et al., 2021; Moral-Rodríguez et al., 2020; Pérez-Cadenas et al., 2009; Segovia-Sandoval et al., 2020; Vivo-Vilches et al., 2018).

The carbonization of the organic xerogel constitutes the final stage of synthesis and plays a fundamental role in developing the microporosity of the carbon xerogel. In this stage, the xerogel undergoes an initial thermal stabilization process to eliminate water residues or unreacted reagents present during synthesis. Thermal stabilization occurs at temperatures ranging from 100 to 200 °C, resulting in a hydrophilic xerogel with elevated oxygen content. Carbonization involves exposing the organic xerogel to an inert gas stream, such as N<sub>2</sub>, He, or Ar, at elevated temperatures ranging from 600 to 1000 °C, using a slow heating ramp. During this process, a significant amount of

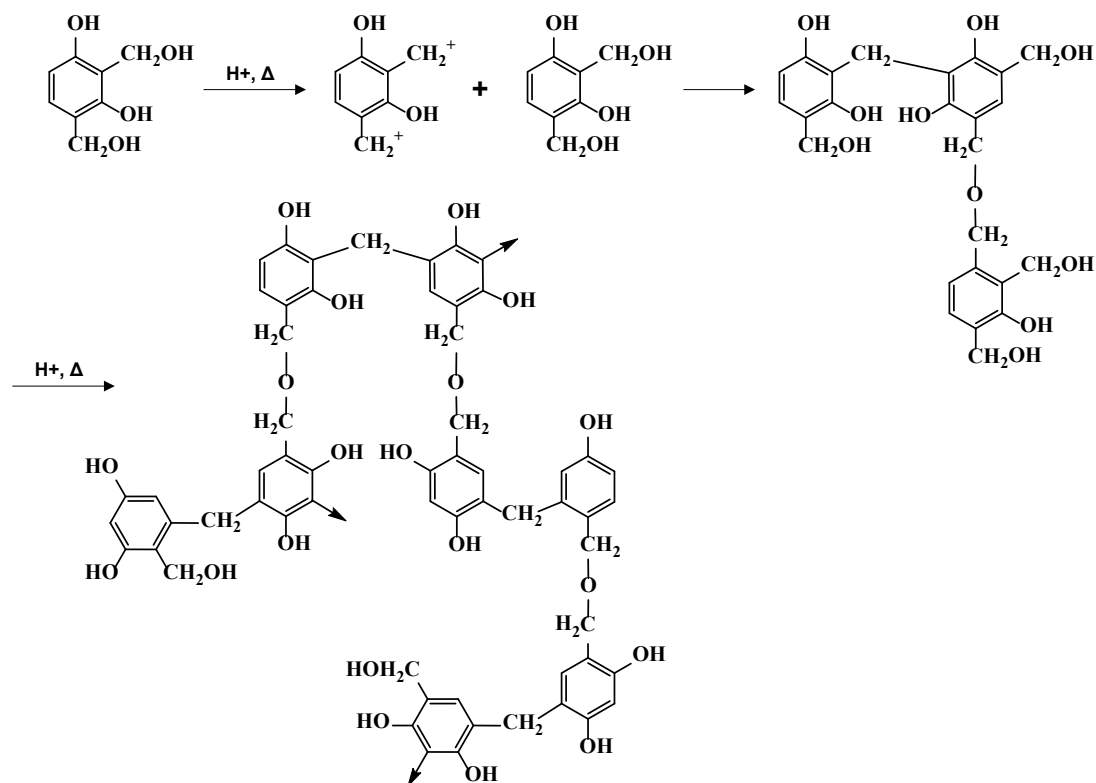


oxygen is removed, resulting in a thermally stable nanostructured carbon xerogel with well-developed microporosity, without altering the structural design established during the sol-gel polymerization.

### 1. Addition reaction



### 2. Condensation reaction



**Figure 2.8.** Polymerization mechanisms of resorcinol and formaldehyde (Arenillas and Fernández, 2022).

The carbon xerogel can undergo an activation process, either chemical or physical, to increase its microporosity and, consequently, its specific surface area. Chemical activation involves impregnating the carbon xerogel with activating chemicals such as  $\text{H}_3\text{PO}_4$ ,  $\text{KOH}$ ,  $\text{ZnCl}_2$ ,  $\text{NaOH}$ , among others, followed by thermal treatment at

temperatures ranging from 400 to 850 °C. This process has certain disadvantages, including the use of high concentrations of activating agent, the need for additional washes to recover the activating agent, and the possibility of partial material dissolution. On the other hand, physical activation is the most commonly used method and is based on controlled thermal treatment of the carbon xerogel with oxidizing agents such as CO<sub>2</sub> or water vapor. This treatment is carried out at temperatures ranging from 700 to 900 °C.

The sol-gel polymerization is a technique that allows obtaining carbon xerogels in various forms, such as microspheres (Bailón-García et al., 2014), films (Espinosa-Iglesias et al., 2015), pellets (Moral-Rodriguez et al., 2020), monoliths (Morales-Torres et al., 2012), and microbeads (Eskenazi et al., 2018). Monolithic carbon xerogels offer numerous advantages compared to other forms, such as low pressure drops, especially at high fluid flows, a larger exposed external surface area, greater accessibility to active sites, and a reduction in mass transport limitations. Therefore, these novel and highly promising materials are very interesting for a wide range of applications, including catalysis, adsorption, and energy storage.

Integral carbon xerogel monoliths are nanostructured porous materials, characterized by a single structure composed of thin, vertical, parallel channels separated by walls and a complex network of macropores that reduce flow resistance. However, existing technology has limited the geometry of these channels. Traditionally, extrusion has allowed the development of monoliths with straight channel geometry, resulting in laminar fluid flow through the channels and limited contact between the fluid and active sites (Morales-Torres et al., 2012; Moreno-Castilla and Pérez-Cadenas, 2010). To improve this aspect, the design of complex or tortuous channels has been explored, inducing turbulent fluid flow within the channels and significantly increasing contact between the fluid and the active sites of the monolith (Chaparro-Garnica et al., 2021a, 2021b). This has sparked great interest in the development of new technologies that allow designing and shaping channels with complex, specific, and highly controlled geometries.

The combination of 3D printing technology with sol-gel polymerization offers an innovative strategy for synthesizing integral carbon xerogel monoliths with a controlled channel configuration. In this method, 3D printed templates with a suitable architectural design of channels are used, which are placed in molds during the first stage of the sol-gel polymerization. During the carbonization process, the template is removed from the xerogel structure, resulting in the formation of the carbon monolith and the shaping of channels with the designed geometry.

The adsorption of pharmaceutical compounds on carbon xerogels has been the subject of limited research. Nevertheless, some studies have yielded promising results. Moral-Rodriguez et al. (2020) investigated the impact of the resorcinol/catalyst molar ratio (R/Cat) on the adsorption of diclofenac in aqueous solution using carbon xerogel pellets. They observed that the highest adsorption capacity was achieved with an R/Cat ratio of 500, reaching an adsorption capacity of 184.6 mg/g at pH = 7. This material exhibited a larger volume and mesoporous area, favoring  $\pi$ - $\pi$  dispersive interactions. In another study, Segovia-Sandoval et al. (2020) explored the adsorption of metronidazole on hybrid materials of carbon xerogels and graphene (CX-GO). They found that the adsorption capacity of CX-GO for metronidazole significantly increased with the increment of graphene content. The maximum adsorption capacity was 160 mg/g in CX-1.0GO, where the number indicates the graphene oxide content. This increase in adsorption capacity was attributed to the rise in the BET area, promoting  $\pi$ - $\pi$  dispersive interactions. Carabineiro et al. (2012) compared the adsorption capacities of activated carbons (AC), carbon xerogels (CX), and carbon nanotubes (CNT) for ciprofloxacin adsorption. They found that the maximum adsorption capacity was obtained in AC (230 mg/g), followed by CNT and CX in decreasing order. This decrease in adsorption capacity is directly related to the BET area of the carbonaceous materials.

Until now, there has been a notable absence of studies exploring the application of 3D printing technology for the fabrication of carbon monolith adsorbents with precisely controlled channel morphologies, specifically designed for the removal of pharmaceutical compounds from water. This unexplored field represents an exceptionally intriguing area of research, distinguished by its low cost, straightforward

handling, and potential for industrial scalability, particularly in the context of continuous adsorption systems. The novelty of this research direction not only underscores its scientific significance but also emphasizes its practical appeal, offering a promising platform to address water pollution challenges associated with pharmaceutical contaminants.

## **2.6 Objectives**

### **2.6.1 General objective**

The aim of this thesis is to develop clay-based adsorbent materials and to fabricate nanostructured carbon monolith adsorbents with controlled porosity and channel morphologies using 3D printing technology combined with sol-gel polymerization, both for the removal of pharmaceutical compounds from aqueous solutions.

### **2.6.2 Specific objectives**

The objectives are described as follows:

- i) Investigate the influence of structural characteristics and nature of diverse raw clays (sepiolite, vermiculite, bentonite, halloysite, phlogopite and kaolinite) on their adsorption capacity for tetracycline from aqueous solutions.
- ii) Examine the impact of the chemical, textural, and swelling properties of bentonite on the adsorption of trimethoprim and chlorphenamine from water.
- iii) Elucidate the mass transport mechanisms controlling the overall adsorption rates of three pharmaceutical compounds, trimethoprim, tetracycline and chlorphenamine on natural bentonite clay.
- iv) Analyze the binary adsorption of tetracycline and cadmium (II) on natural bentonite clay under different solution pH conditions and elucidate the binary adsorption mechanisms.
- v) Synthesize hybrid clay-based adsorbents through a cation exchange reaction with hexadecyltrimethylammonium bromide and investigate the impact of surface chemistry on the adsorption capacity for several pharmaceuticals,

including carbamazepine, tetracycline, sulfamethoxazole and chlorphenamine, each possessing different chemical properties.

- vi) Optimize the synthesis conditions of carbon xerogels to achieve synthetic materials with tailored morphology and well-defined pore size distributions, specifically designed for the removal of sulfamethoxazole from water.
- vii) Design and fabricate integral carbon xerogel monoliths with precisely engineered channel geometries, utilizing a combination of sol-gel polymerization with 3D printing technology, for the efficient removal of sulfamethoxazole from water. Furthermore, evaluate the impact of synthesis conditions on adsorption performance.
- viii) Investigate the effect of CO<sub>2</sub> and H<sub>2</sub>O activation time on the chemical and textural properties of carbon monoliths and evaluate its influence on the adsorption of sulfamethoxazole from aqueous phase.
- ix) Explore the effects of diverse channel geometries on breakthrough curves for the adsorption of sulfamethoxazole from aqueous solutions and corroborate the results with Computational Fluid Dynamics (CFD) calculations.

# CHAPTER

EXPERIMENTAL METHODS

3

### **3.1 Preparation and synthesis of clay-based materials and carbon monolithic structures**

#### **3.1.1 Clay minerals preconditioning**

Calcium bentonite was sourced from a mineral deposit in San Luis Potosi, Mexico. Vermiculite was supplied by Virginia Vermiculite Company, Louisa, Virginia, USA. Phlogopite was obtained from RENAGO in Oaxaca de Juarez, Oaxaca, while kaolinite, sepiolite and halloysite were provided by Synerplus, Sepiolsa and Merck, respectively. All clay minerals were ground and sieved to -200 +400 mesh sizes. The preconditioning of the clay is described in Chapter 4, Section 4.4.2.

#### **3.1.2 Preparation of clay samples with different uptakes of pharmaceuticals adsorbed**

Clay samples were saturated with pharmaceuticals at various adsorption levels. The nomenclature and specifications of these prepared samples are detailed in Chapter 5, Table 5.2.

#### **3.1.3 Synthesis of hybrid hexadecyltrimethylammonium bromide-modified organobentonite**

Organobentonite was prepared through a cation exchange reaction between bentonite and the cationic surfactant hexadecyltrimethylammonium bromide. The detailed methodology is outlined in Chapter 8, Section 8.2.1.

#### **3.1.4 Synthesis of nanostructured carbon xerogels**

Nanostructured carbon xerogels were synthesized through sol-gel polymerization of resorcinol and formaldehyde, with  $\text{Cs}_2\text{CO}_3$  as a catalyst. The synthesis involved varying the resorcinol/catalyst ratios to modulate gel porosity. A detailed synthesis method is provided in Chapter 9, Section 9.2.1.

### **3.1.5 Design of 3D geometries using Computer-Aided Design (CAD)**

Detailed prototypes of 3D CAD models were developed using Solid-Works software to accurately represent the channel geometries of monoliths. The design methodology is detailed in Chapter 11, Section 11.2.1.

### **3.1.6 Fabrication of 3D-printed carbon monoliths**

A hybrid method that combining sol-gel polymerization with advanced 3D printing technology was used to fabricate 3D-printed carbon monoliths. This innovative hybrid method is discussed in Chapter 10, Section 10.2.2.

### **3.1.7 Activation of 3D-printed carbon monoliths using CO<sub>2</sub> and H<sub>2</sub>O**

The 3D-printed carbon monoliths were activated using CO<sub>2</sub> and H<sub>2</sub>O at 850 °C. The activation procedures are detailed in Chapter 11, Section 11.2.3.

## **3.2 Characterization techniques**

The characterization of clay-based materials and 3D-printed carbon monoliths involved techniques such as CO<sub>2</sub> adsorption, N<sub>2</sub> adsorption, Hg intrusion porosimetry, SEM, XRD, FT-IR, thermogravimetric analysis, XPS, Zeta potential, helium pycnometry, cation exchange analysis, determination of acidic and basic sites, point of zero charge and stress-strain experiments. Each technique is discussed in the chapters of this thesis.

## **3.3 Adsorption tests**

Adsorption tests were conducted in both batch and continuous operations. Experimental adsorption data were collected using a batch adsorption system, a stirred tank batch adsorber for suspended particles and a monolithic packed bed adsorber. The operating conditions included pH, temperature, ionic strength, initial concentration, stirring speed, volumetric flow rate, and the channel geometries of the 3D-printed monoliths. Detailed descriptions of each operation are provided in the corresponding chapters.



# CHAPTER

# 4

**REMOVAL OF TETRACYCLINE  
FROM AQUEOUS SOLUTIONS BY  
ADSORPTION ON RAW Ca-  
BENTONITE. EFFECT OF  
OPERATING CONDITIONS AND  
ADSORPTION MECHANISM**

## **4.1 Introduction**

Human, industrial and agricultural activities contribute significantly to environmental pollution. Nowadays, great concern has been arisen due to the occurrence and detection of various toxic organic compounds of anthropogenic origin in water resources. These new chemicals, known as emerging pollutants or contaminants of emerging concern, have commonly used as personal care products, drugs, pesticides, hormones, among others. These compounds are continuously discharged into water resources, causing persistence and bioaccumulation, and can pose a hazardous threat to human beings and the environment (Wilkinson et al., 2017).

Tetracycline (TC) is a wide-spectrum antibiotic having high activity toward an ample variety of microorganisms. TC is also commonly employed to stimulate the growth rate and boost the feed efficiency of animals because of its low cost (Chopra and Roberts, 2001; Gao et al., 2012). TC has been detected in surface waters (rivers, lakes and seawater), groundwater, drinking water, sediments and wastewater and sludge (Xu et al., 2021). The concentrations of TC in surface waters and effluents from wastewater treatment plants fluctuated from 0.0011 to 110 µg/L and 0.001 to 3170 µg/L, respectively (Xu et al., 2021).

Diverse removal processes have been examined for eliminating TC in water solutions, inclusive of advanced oxidation processes. The heterogeneous photocatalysis of TC was achieved using TiO<sub>2</sub> (Maroga Mboula et al., 2012), and the results showed that TC was partially mineralized, generating by-products with low biodegradability and less toxicity than TC. Furthermore, the TC ozonation in a water solution was also investigated in the pH range of 2.2-7, and it was found that the aromatic rings and the dimethylamino group of the TC produced recalcitrant by-products during the ozonation. After 2 h, the degradation percentage of TC was 40 % (Khan et al., 2010). In a recent study, TC was photodegraded by UV irradiation and a new sulfate radical, UV/peroxymonosulfate; however, after irradiation, the solution's toxicity significantly increased due to the formation of various toxic by-products (Ao et al., 2019).

Among the alternative and promising methods for treating contaminated aqueous effluents, adsorption has attracted much consideration because of its outstanding features like simple and economical process, high removal efficiency, and without generating noxious by-products (Yu et al., 2016). Different adsorbents, varying from natural minerals to advanced nanostructured materials, have been applied in this separation method.

In several works, different carbonaceous materials were synthesized and applied for adsorbing TC. Gao et al. (2012) applied graphene oxide for adsorbing TC from water, and the results revealed that the adsorption occurred by physical and chemical interactions, and the maximum mass adsorbed of TC was 313 mg/g. Ji et al. (2009) analyzed the TC adsorption onto multiwalled carbon nanotubes (MWCNTs), and the results showed that TC was adsorbed on MWCNTs by the  $\pi$ - $\pi$  dispersive interactions, resulting in the maximum capacity of 100 mg/g. Furthermore, Rivera-Utrilla et al. (2013) determined the adsorption capacity of granular activated carbon towards TC to be 375.4 mg/g, and the primary adsorbing mechanism was the electrostatic interactions between the TC species in solution and the carbon surface.

Among the natural adsorbents, clay minerals have several outstanding characteristics: mesoporous structure, negatively charged surface, specific surface area, hydration, swelling, high cation exchange capacity and chemical stability, which favors the adsorption of a wide variety of pollutants. Bentonite is a raw clay mainly composed of montmorillonite ( $\text{Na}_{0.6}(\text{Al}_{3.4}\text{Mg}_{0.6})\text{Si}_8\text{O}_{20}(\text{OH})_4$ ) that belongs to the smectite group. Its trilaminar structure (2:1) is formed by one  $\text{Al}^{3+}$  octahedral sheet placed between two  $\text{Si}^{4+}$  tetrahedral sheets. The negatively charged surface of bentonite is mainly counterbalanced by  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , designated as exchangeable cations (Leyva-Ramos et al., 2021).

The TC adsorption on clay minerals has been studied in few works; however, the TC adsorption on bentonite has not been analyzed thoroughly, and neither has the mechanisms of TC adsorption been explained. Some studies have shown that montmorillonite exhibited a reasonable affinity towards TC. The sodium and calcium montmorillonites have been applied for removing TC (Parolo et al., 2013), and at pH =

3, the calcium montmorillonite presented a maximum mass of TC adsorbed of 315.5 mg/g. Zhao et al. (2012) determined the montmorillonite capacity for adsorbing TC to be 250 mg/g at pH = 5.5. Iron-intercalated montmorillonite was synthesized to remove TC and presented a maximum mass of TC adsorbed of 290 mg/g at pH = 5. This high capacity was due to the increment in the pore volume and specific surface area, originated by intercalating of iron-(hydr)oxide in the montmorillonite interlaminar space (Wu et al., 2016). Current studies claim that high affinity of TC can be ascribed to the TC intercalation in the interlaminar space of montmorillonite; however, detailed studies refer to the interactions between TC and bentonite, and the adsorption mechanisms at acid and neutral conditions are even scarcer.

Chapter 4 presents the TC adsorption upon various raw clay minerals, including diverse structural characteristics, and the raw bentonite (Bent) exhibited the highest adsorption capacity towards TC. The characterization of Bent and TC adsorbed onto Bent was carried out by various analytical techniques. The solution ionic strength, temperature, and pH influence in Bent capacity for adsorbing TC was also analyzed thoroughly. Furthermore, the reversibility of the TC adsorption on bentonite was examined in detail. The adsorption mechanisms of TC on bentonite in acid and neutral aqueous medium were also explained in detail.

## **4.2 Experimental methodology**

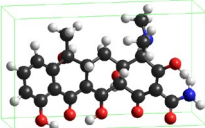
### **4.2.1 Materials**

The calcium bentonite (Bent) was obtained from a mineral deposit in San Luis Potosi, Mexico. Virginia Vermiculite Company, Louisa, Virginia, USA, supplied vermiculite (Verm). The phlogopite (Phlo) was provided by the company RENAGO located in Oaxaca de Juarez, Oaxaca. Synerplus, Sepiolsa (Spain) and Merck supplied the kaolinite (Kaol), sepiolite (Sep) and halloysite (Hal), respectively.

The chemical structure TC is illustrated in Figure 4.1 (a), and Table 4.1 lists its physicochemical characteristics. TC can exist in four distinct species in aqueous solution, and the speciation diagram of TC is affected by the pH and is displayed in Figure 4.1 (b). This figure shows that the TC cationic species ( $TC^+$ ) predominates at

pH lesser than 3, the neutral or zwitterionic species ( $TC^{\pm}$ ) prevails in a pH interval from 3 to 7, and the anionic species ( $TC^{-}$  and  $TC^{2-}$ ) are predominant at pH higher than 7.

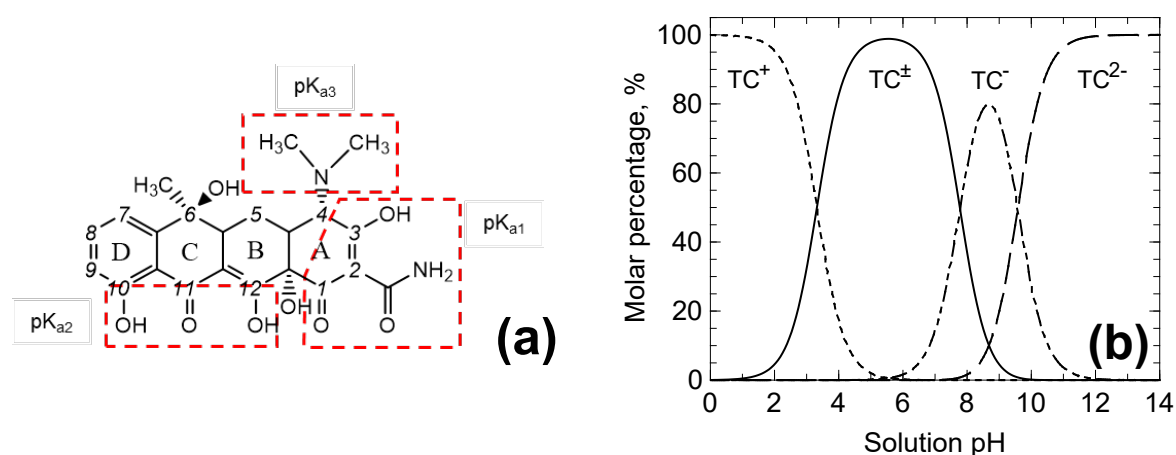
**Table 4.1.** Physicochemical properties of TC.

| Pharmaceutical compound               | Family      | Molecular structure <sup>a</sup>                                                  | Molecular size <sup>a</sup><br>(nm) | Log D <sup>b</sup> | pK <sub>a</sub> <sup>c</sup> |
|---------------------------------------|-------------|-----------------------------------------------------------------------------------|-------------------------------------|--------------------|------------------------------|
| Tetracycline<br>(TC)<br>M.W. = 444.44 | Antibiotics |  | X = 1.38<br>Y = 0.81<br>Z = 0.69    | -1.30              | 3.32,<br>7.78,<br>9.58       |

<sup>a</sup> Determined by Density Functional Theory (DFT) using B3LYP method.

<sup>b</sup> Distribution coefficient at pH = 7.

<sup>c</sup> Dissociation constants (Chopra and Roberts, 2001).



**Figure 4.1.** Chemical structure of TC (a) and speciation diagram of TC (b) as a function of solution pH.

#### 4.2.2 Clay minerals preconditioning

The clay minerals were ground in an analytical mill, IKA, A 11 basic model, and sieved using -200 +400 mesh sizes, corresponding to a mean particle size of 0.056 mm. Afterward, the ground clays were rinsed various times with deionized water, separated from the washing medium by decantation, dried for 24 h at 110°C and placed in sealed containers.

#### **4.2.3 Characterization of bentonite and bentonite with TC adsorbed**

The clay mineral samples were designated as Bent, B-TC (pH 3) and B-TC (pH 7), referring to raw bentonite and bentonite saturated with TC at pH of 3 and 7, and the corresponding loading of TC was  $q = 257.2$  and  $153.3$  mg/g, respectively. The physicochemical properties of clay mineral samples were determined by various analytical techniques. The chemical composition of Bent expressed as a weight percentage of the constituent oxides is presented in Table 4.2 (Martinez-Costa and Leyva-Ramos, 2017).

The textural characteristics were evaluated using the N<sub>2</sub> adsorption-desorption isotherm, appraised in an N<sub>2</sub> physisorption analyzer, Micromeritics, ASAP 2020 model. The Brunauer, Emmett and Teller (BET) method was employed to evaluate the specific surface area,  $S_{BET}$  (Brunauer et al., 1938). Besides, the area of the mesopores,  $S_{meso}$ , was computed by the t-plot method. The Barret-Joyner-Halenda (BJH) procedure was applied to estimate the pore size distribution and the total accumulated pore volume (Barrett et al., 1951). The total volume of the pores,  $V_p$ , and the volume of the mesopores,  $V_{meso}$ , were assessed from the pore size distribution by the computational procedures recommended by Rouquerol et al. (1998). The average pore diameter,  $D_p$ , was estimated using the following equation (Rouquerol et al., 1998):

$$D_p = \frac{4 \times V_p}{S_{BET}} \quad (4.1)$$

The clay mineral morphology was examined in a scanning electron microscope, JEOL, model JSM-6610LV. The procedure suggested by Ming and Dixon (1987) was utilized to determine the cation exchange capacity (CEC). The procedure consists of the following steps: i) Saturation of the bentonite with Na<sup>+</sup> cations, ii) Exchange of Na<sup>+</sup> cations by NH<sub>4</sub><sup>+</sup> cations, and iii) Determination of Na<sup>+</sup> cations released from the bentonite to the solution. The crystalline phases of a sample were identified in a Rigaku diffractometer, model DMAX 2000, under operating conditions of Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm), 30 mA and 30 kV. The diffractometer was programmed to carry out a scan from 4 to 45 ° (2 $\theta$ ) and using a step of 1.8 °/min. The coexisting phases were

identified by comparing their standards compiled by the International Center of Diffraction Data (ICDD).

The thermogravimetric analysis of the Bent, B-TC (pH 3) and B-TC (pH 7) was conducted in a Perkin Elmer analyzer, Pyris Diamond, TGA/DTA model, and the operating conditions were temperature range 25-1000°C and a heating rate of 10°C/min. The Zeta potential of Bent surface in water solution was determined in a Zetameter, Zetasizer 4 model, following the next procedure. Bent dispersions (0.01 g of particles/50 mL) were prepared in 50 mL centrifuge vials by adding Bent and the solutions of constant ionic strength (0.01 N) in the pH interval from 2 to 12, fixed by mixing appropriate aliquots of 0.01 N HCl and NaOH solutions. The vials containing the dispersions were set in a water bath at 25°C, and the pH was adjusted daily. The dispersions were mechanically stirred. After eight days, an aliquot (1 mL) was taken to quantify the Zeta potential of the Bent. Moreover, the Zeta potential of B-TC (pH 3) and (pH 7) was determined as a function of the uptake of TC adsorbed on Bent, using TC concentrations from 15 to 120 mg/L.

#### **4.2.4 Quantification of TC concentration in water samples**

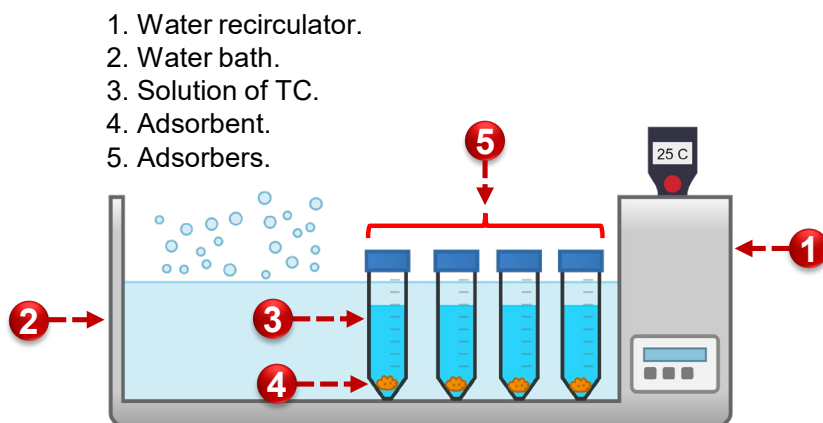
A UV-Vis spectrophotometry procedure was implemented to assess the TC concentration in aqueous samples. The sample absorbance was ascertained in a Shimadzu spectrophotometer, 2600 model, set up at the specific wavelength of 357. The TC concentration was calculated using calibration curves prepared from TC standard solutions having concentrations from 0.6 to 42 mg/L and pH of 7, 5 or 3.

#### **4.2.5 Technique for conducting the adsorption equilibrium experiments**

In this work, a stock solution of TC (300 mg/L) was prepared by dissolution of a certain mass of TC (2.19 g) using a solution having a constant ionic strength of 0.01 N and pH of 3, 5, or 7. 1 L, which was made by mixing the proper volumes of 0.01 N HCl and NaOH solutions fixed with deionized water.

A batch adsorber consisting of a centrifuge vial (50 mL) was utilized to conduct the TC adsorption experiments on the clay (Figure 4.2). The TC solutions of known

initial concentration, 30-250 mg/L, were formulated by adding a given aliquot of the TC stock solution into a volumetric flask (50 mL) and then diluting using the solution with a constant ionic strength ( $I = 0.01\text{ N}$ ) and a particular pH. Later, 40 mL of these solutions were added to, named batch adsorbers, containing a certain mass of the clay. The solution temperature was kept constant by placing the adsorber in a thermostatic bath, and the adsorber was placed in a rotary shaker for stirring the solution for 40 min every day. The pH was determined daily and maintained constant by supplementing drops of NaOH and HCl solutions (0.01, 0.1 and 1 N). In the adsorption runs, it was noticed that the solution pH diminished when the initial pH was 7 but increased when the initial pH was 3 or 5. Thus, the solution had to be kept constant because the adsorption equilibrium depended on the solution pH. The initial volume of the solution was considered constant because the supplemented volume was invariably less than 2.0 % of the initial volume.



**Figure 4.2.** Batch adsorbers.

In preliminary runs, the solution was sampled at predetermined times, and the TC concentration in each sample was determined. Equilibrium was assumed to be reached when the TC concentrations of two consecutive samples did not change significantly. The results of the preliminary runs showed that 7 days were enough to attain equilibrium. After eight days, once equilibrium was achieved, the dispersions were centrifuged at 2500 rpm during 10 min. Subsequently, an aliquot (5 mL) was



filtered to determine the TC concentration. Then, the uptake adsorbed of TC was computed from the succeeding equation:

$$q = \frac{V}{m}(C_o - C_e) \quad (4.2)$$

where  $C_e$  and  $C_o$  are the TC equilibrium and initial concentrations, mg/L;  $m$  is the amount of clay mineral, g;  $q$  is the mass adsorbed of TC, mg/g;  $V$  is the TC solution volume, L.

#### **4.2.6 Technique for performing the desorption equilibrium experiments**

Once equilibrium was attained, according to the conditions outlined previously, the desorption experiments were carried out. The Bent equilibrated with TC was extracted from the solution and subsequently transferred to another adsorber holding a solution without TC (40 mL) with a particular ionic strength and pH. The pH was measured and adjusted daily, as described above. Upon reaching desorption equilibrium (eight days), a 5 mL aliquot was filtered to quantify the concentration of TC. The amount of TC not desorbed was assessed from the following equation:

$$q_d = q_o - \frac{V}{m}C_{ed} \quad (4.3)$$

where  $C_{ed}$  is the concentration of TC at equilibrium in the desorption experiment,  $q_o$  is the uptake of TC adsorbed starting the desorption experiment, mg/g;  $q_d$  represents the uptake of TC that did not desorb in the desorption run, mg/g.

#### **4.2.7 Procedure for determining the amounts of cations adsorbed during adsorption of TC**

The method consisted of two steps. In this first one, the Bent was allowed to equilibrate with the solution without TC. A solution (pH of 3 or 7,  $I = 0.01$  N) volume was poured into a batch adsorber, and the Bent dosage was 30 mg/40 mL (pH = 3) and 50 mg/40 mL (pH = 7), soon afterward, the adsorber was partially submerged in a thermostatic bath, mechanically shaken, and adjusting the solution pH to maintain it constantly. After 8 days, the pH was determined, and the solution was sampled (1 mL) to quantify by Atomic Absorption spectrometry the exchangeable cation concentrations

(Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) in the solution before TC adsorption. In the second step, the adsorption of TC was carried out by supplementing an aliquot of a TC solution with a specific concentration to make the initial TC concentration equal to 250 mg/L in the adsorber solution. Promptly, the pH was measured and designated as pH<sub>in</sub>, and the concentrations of the exchangeable cations were corrected due to adding the aliquot, and these concentrations were designated as C<sub>i0</sub>. After eight days in contact, the solution's final pH (pH<sub>fn</sub>) was registered, and the final concentrations of cations, C<sub>if</sub>, and TC in this solution were quantified.

The equivalents of cations adsorbed or desorbed were determined by performing an equivalents balance, similar to the mass balance represented by Equation (4.2). The overall uptake of TC adsorbed due to various mechanisms as well as the uptakes of H<sup>+</sup> and exchangeable cations adsorbed were computed by the succeeding equations (Salazar-Rabago and Leyva-Ramos, 2016).

$$Q_{TC} = \frac{q_e \times 100}{EW_{TC}} \quad (4.4)$$

$$Q_{H^+} = \frac{(10^{-pH_{in}} - 10^{-pH_{fn}}) \times 1000 \times V \times 100}{m} \quad (4.5)$$

$$Q_i = \frac{(C_{i0} - C_{if}) \times 1000 \times V \times 100}{m} \quad (4.6)$$

where C<sub>if</sub> and C<sub>i0</sub> are the final and initial concentrations of the exchangeable cation *i*, eq/L; EW<sub>TC</sub> is the equivalent weight of TC, 444.44 g/eq; Q<sub>TC</sub> is the uptake of TC adsorbed on Bent, cmol(+)/kg; Q<sub>H<sup>+</sup></sub> and Q<sub>i</sub> are the uptakes of H<sup>+</sup> and exchangeable cation *i* adsorbed by ion exchange, cmol(+)/kg; pH<sub>fn</sub> and pH<sub>in</sub> are the final and initial pH values of the solution, and V represents the TC solution volume in the adsorber, L. It is essential to mention that Q<sub>H<sup>+</sup></sub> and Q<sub>i</sub> would be positive if the H<sup>+</sup> and exchangeable cations were adsorbed on Bent, whereas they would be negative if the H<sup>+</sup> and exchangeable cations were desorbed from Bent.

The total uptake of cations (exchangeable cations and H<sup>+</sup>) adsorbed during the adsorption of TC on Bent was computed as follows:

$$Q_{T,Cat} = Q_{H^+} + \sum Q_i \quad (4.7)$$

### 4.3 Results and discussion

#### 4.3.1 Cation exchange capacity, chemical composition, textural characteristics and morphology of bentonite

The CEC, chemical composition and textural properties of Bent are registered in Table 4.2. The CEC of Bent was determined to be 75.2 cmol(+)/kg. This CEC value is within the CEC interval for bentonite reported in the literature, 70-140 cmol(+)/kg (Borden, 2001; Wang et al., 2010). As seen in Table 4.2, the weight percentage of the constituent oxides showed that the mineral clay used in this work is calcium bentonite due to the content of CaO (3.26%).

**Table 4.2.** Chemical composition and textural properties of Bent and B-TC (pH 3).

| Chemical composition of Bent   |            | Textural properties and CEC                         |       |             |
|--------------------------------|------------|-----------------------------------------------------|-------|-------------|
|                                | (% weight) | Property                                            | Bent  | B-TC (pH 3) |
| SiO <sub>2</sub>               | 65.70      | S <sub>BET</sub> <sup>a</sup> (m <sup>2</sup> /g)   | 45    | 13          |
| Al <sub>2</sub> O <sub>3</sub> | 19.60      | V <sub>p</sub> <sup>b</sup> (cm <sup>3</sup> /g)    | 0.087 | 0.063       |
| Fe <sub>2</sub> O <sub>3</sub> | 3.73       | D <sub>p</sub> (nm)                                 | 7.8   | 19.7        |
| K <sub>2</sub> O               | 2.88       | S <sub>meso</sub> <sup>c</sup> (m <sup>2</sup> /g)  | 32    | 13          |
| CaO                            | 3.26       | V <sub>meso</sub> <sup>d</sup> (cm <sup>3</sup> /g) | 0.075 | 0.046       |
| MgO                            | 3.73       | CEC <sup>e</sup> (cmol(+)/kg)                       | 75.2  | -           |
| Na <sub>2</sub> O              | 0.79       |                                                     |       |             |

<sup>a</sup> Specific surface area determined by the BET method.

<sup>b</sup> Total pore volume evaluated by the BJH method.

<sup>c</sup> Mesoporous area calculated by the “t-plot” method.

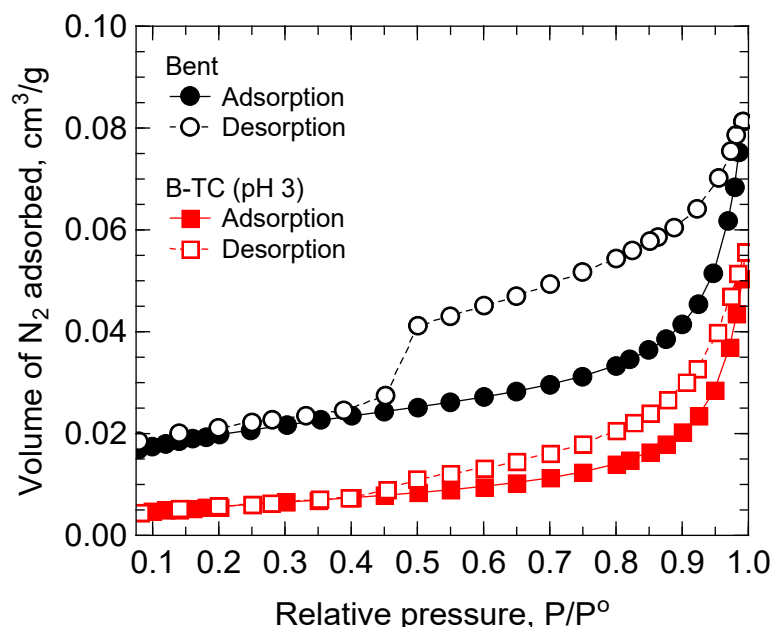
<sup>d</sup> Mesoporous volume obtained by the BJH method.

<sup>e</sup> CEC evaluated by the method proposed by Ming and Dixon (1987).

The D<sub>p</sub>, S<sub>BET</sub>, V<sub>p</sub> and V<sub>meso</sub> of Bent were 7.8 nm, 44.5 m<sup>2</sup>/g, 0.087 cm<sup>3</sup>/g and 0.075 cm<sup>3</sup>/g, correspondingly. These values agree with those reported for raw bentonites (Moma et al., 2018; Moraes et al., 2011). The S<sub>BET</sub>, V<sub>p</sub> and V<sub>meso</sub> for B-TC (pH 3) decreased to 13 m<sup>2</sup>/g, 0.063 cm<sup>3</sup>/g and 0.046 cm<sup>3</sup>/g, correspondingly, and D<sub>p</sub> increased from 7.8 to 19.7 nm, after the TC adsorption on Bent. The significant

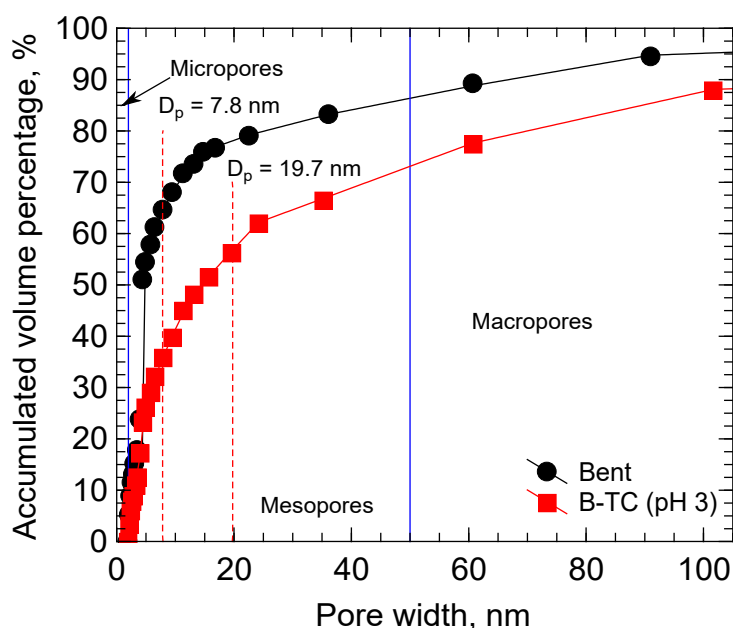
decrease in  $S_{\text{BET}}$ ,  $V_p$  and  $V_{\text{meso}}$  can be attributed to the filling up and blocking off the mesopores by the TC molecules adsorbed.

Figure 4.3 depicts the  $\text{N}_2$  adsorption-desorption isotherms on Bent and B-TC (pH 3), and the two isotherms are of type IIb, characteristic of clays or aggregates of platy particles. According to the IUPAC classification, both isotherms show a hysteresis loop of type H3, characteristic of mesoporous materials (Sing, 1985). The mesoporous structure of this type of clays is due to the interparticle spaces produced by the disorderly arrangement of the clay sheets (Domínguez and Schifter, 1992). The B-TC (pH 3) displays a narrower hysteresis loop, indicating that its mesopores were obstructed after the TC adsorption on the pore surface of Bent.



**Figure 4.3.** Adsorption-desorption isotherms of  $\text{N}_2$  on Bent and B-TC (pH 3) at  $-196.15\text{ }^{\circ}\text{C}$ .

The cumulative pore volume percentage for Bent and B-TC (pH 3) are displayed in Figure 4.4. As seen in this figure, the Bent and B-TC (pH 3) are mainly composed of mesopores because the mesopore volume represents 86 and 73 % of the total pore volume, respectively. The mesopore volume of B-TC (pH 3) was reduced after adsorption of TC, suggesting that TC adsorption is mainly occurring in the mesopores. This result also explains why the  $D_p$  of B-TC (pH 3) is higher than the  $D_p$  of Bent.

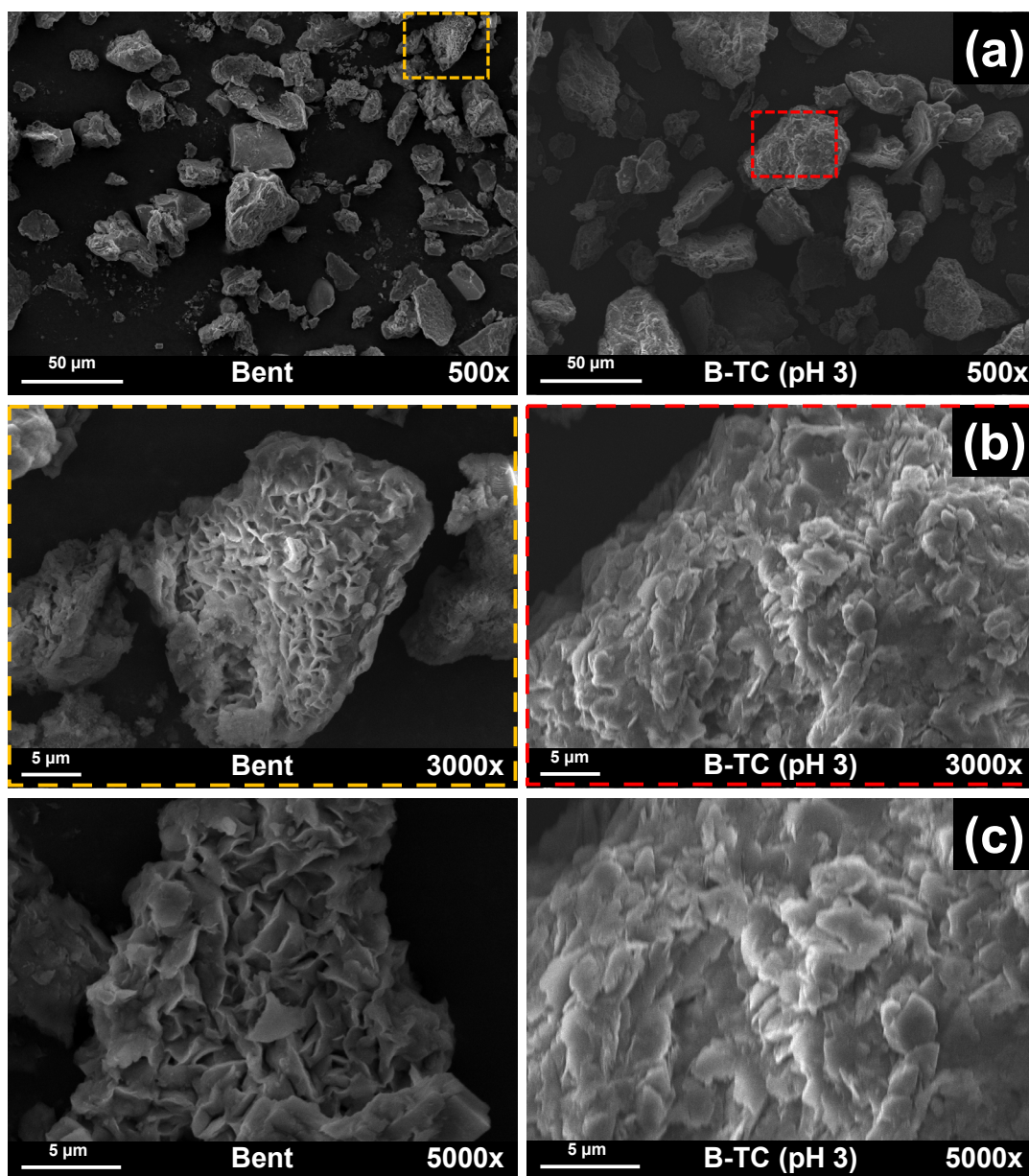


**Figure 4.4.** The cumulative pore volume percentage of Bent and B-TC (pH 3).

Figure 4.5 (a) shows an overall view of Bent and B-TC (pH 3) particles by SEM. Morphology of clay can be observed in detail at higher magnifications (areas selected by yellow and red dashed lines). Bent shows flatty particles stacked randomly typical of an open-textured Ca-montmorillonite, Figure 4.5 (b) and (c). The morphology changed in B-TC (pH 3), exhibiting bigger particle sizes and adsorbed TC formed dense agglomerates on the external surface of Bent and empty spaces between randomly stacked flatty particles. The SEM analysis confirmed that the adsorption of TC partially took place on the external surface of Bent particles and spaces between particles.

### 4.3.2 Zeta potential distribution

Figure 4.6 (a) depicts the zeta potential distribution of Bent vs. the pH. In the pH interval tested, the Bent presented a negative surface charge, exhibiting more negative zeta potential while increasing the solution pH. The negative charge of Bent is attributed to negative charge deficiency caused by isomorphic substitutions of  $\text{Si}^{4+}$  for  $\text{Al}^{3+}$  and  $\text{Al}^{3+}$  for  $\text{Mg}^{2+}$  or  $\text{Fe}^{2+}$  in the octahedral and tetrahedral sheets, correspondingly (Domínguez and Schifter, 1992).



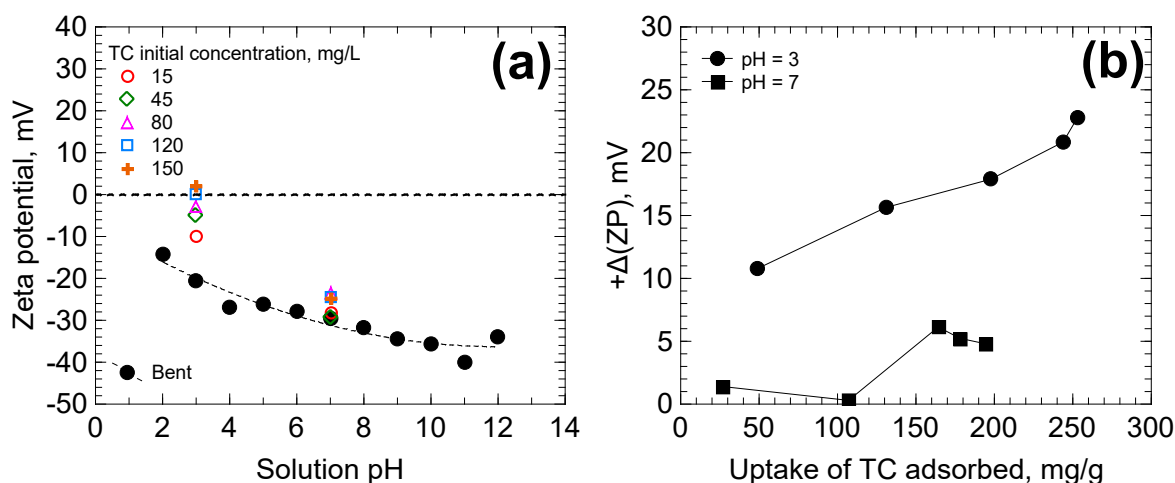
**Figure 4.5.** SEM images of Bent and B-TC (pH 3) recorded at 500X (a), 3000X (b) and 5000X (c).

Furthermore, Figure 4.6 (b) displays that the initial concentration of TC influences the zeta potential at pH = 3 and 7. The TC initial concentration influenced Bent surface charge because the TC adsorbed on Bent surface can balance the surface charge of Bent. Consequently, the uptake adsorbed of TC on Bent grew by

incrementing the initial concentration and was calculated as explained in Section 4.2.5. As seen in Figure 4.6 (a), at pH = 3, the negative surface charge shifted towards less negative values or even positive, while the TC initial concentration or the mass of TC adsorbed raised. In contrast, at pH = 7, there was no significant difference in surface charge of Bent for higher TC initial concentrations. Variations in surface charge can be visualized clearly by calculating the Zeta potential difference  $\Delta(ZP)$  as a function of the uptake of TC adsorbed ( $q$ ). The  $\Delta(ZP)$  was calculated applying the following equation:

$$\Delta(ZP) = (ZP)_{B-TC} - (ZP)_{Bent} \quad (4.8)$$

where  $(ZP)_{B-TC}$  is the zeta potential of bentonite saturated with TC (B-TC), mV, and  $(ZP)_{Bent}$  is the zeta potential of Bent, mV. Figure 4.6 (b) shows the  $\Delta(ZP)$  vs.  $q$ , and as shown in this figure, at pH = 3, the  $\Delta(ZP)$  increased linearly, augmenting the mass of TC adsorbed. On the contrary, at pH = 7, the  $\Delta(ZP)$  showed no significant change as a function of  $q$ .



**Figure 4.6.** Zeta potential distribution of Bent as a function of TC initial concentration (a) and Zeta potential difference of Bent as a function of the uptake of TC adsorbed (b) at  $T = 25\text{ }^{\circ}\text{C}$  and pH of 3 and 7.

The behavior of  $\Delta(ZP)$  at pH = 3 revealed that the adsorption mechanism of TC on Bent depends significantly on the electrostatic attractions since  $\text{TC}^+$  is attracted to negatively charged surface and adsorbed on the cationic sites of Bent, balancing the negative charge of the surface. On the contrary, at pH = 7, the slight variation of  $\Delta(ZP)$

showed no contribution of electrostatic attractions in the adsorption mechanism of TC. Thus, the adsorption of the  $TC^{\pm}$  and  $TC^{-}$  species at pH = 7 may be caused by non-electrostatic interactions, like hydrophobic interactions, formation of coordination complexes or hydrogen bonding (Flores et al., 2017; Ibrahim et al., 2018; Porubcan et al., 1978; Undabeytia et al., 1999; Yamamoto et al., 2018).

#### **4.3.3 X-ray diffraction testing**

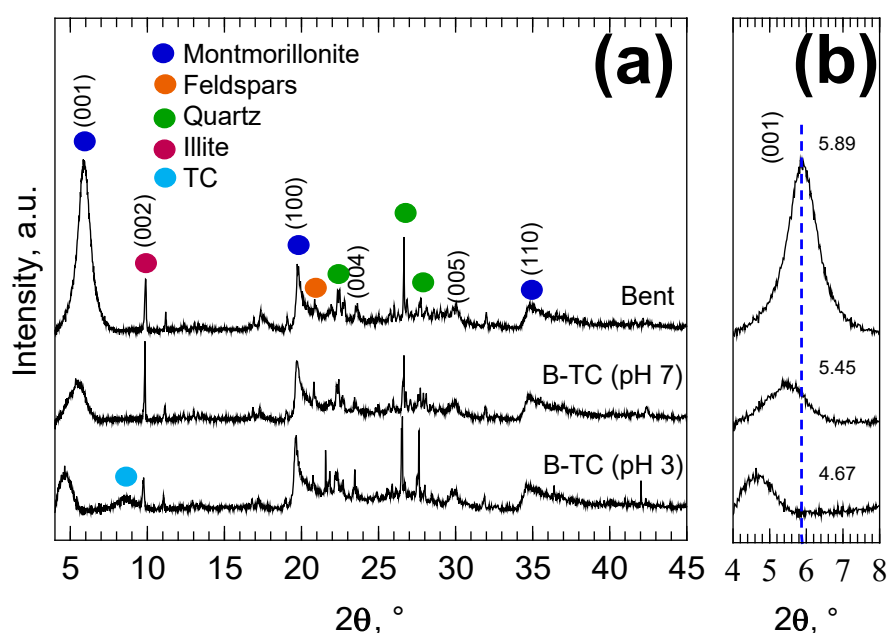
The XRD patterns of Bent, B-TC (pH 7) and B-TC (pH 3) are shown in Figure 4.7. The principal reflections in the XRD pattern of Bent show the crystalline plane with the (001) Miller index at  $5.89^{\circ}$  ( $2\theta$ ) and the reflections at  $19.72$ ,  $23.51$  and  $34.74^{\circ}$  ( $2\theta$ ) which corresponded to the montmorillonite (JCPDS 13-0135) (X. Wang et al., 2015; Y. Wang et al., 2019), corroborating that Bent is mainly composed of montmorillonite. The X-ray pattern of Bent also contains quartz and feldspar reflections, constituting the secondary crystalline compounds in Bent. Besides, the possible coexistence of illite was detected at  $9.8^{\circ}$  ( $2\theta$ ) (Elgamouz et al., 2019).

The plane (001) related to the basal reflection was 1.50 nm in Bent. Usually, the thickness of the 2:1 laminar configuration of the montmorillonite is 0.96 nm (Moore and Hower, 1986). Therefore, the interlayer space in basal reflection (001) observed for Bent, 0.54 nm, is related to the presence of two  $H_2O$  molecules (0.25 nm) between the sheets and associated with the hydration of the interlaminar  $Ca^{2+}$  cation. The estimated basal reflection (001) for B-TC (pH 7) and B-TC (pH 3) were 1.62 and 1.89, corresponding to interlayer spaces of 0.66 and 0.93 nm, correspondingly. According to the TC molecular size (Table 4.1), the interlayer space for the B-TC (pH 3) sample is wide enough to corroborate that the TC molecules are intercalated in the interlayer space of Bent and oriented parallel over their XZ or XY cross-sectional area, or slightly tilted. This result agrees with other studies (Parolo et al., 2013; Wu et al., 2016).

In the B-TC (pH 7) sample, the interlayer space was slightly smaller than the shortest dimension (Z) of the TC molecule. However, it has been reported that the increment in interlaminar space caused by the adsorption of organic molecules can be at least 0.1 nm lesser than the smallest dimension of the adsorbed molecule (Greene-



Kelly, 1955), suggesting that the  $\text{TC}^+$  and  $\text{TC}^-$  species, despite their electric charge, can be partially intercalated in the interlayer space in a tilted orientation over their XY cross-sectional area. Some authors have reported that the intercalation of nitrobenzene, pyridine and benzoic acid can be in the interlayer space of montmorillonite, even though these compounds are neutral species (Farmer and Mortland, 1966; Lu et al., 2010; Yariv et al., 1966). The TC adsorbed on Bent was confirmed only in B-TC (pH 3) due to the identification of its main reflection at about  $8.5^\circ$  ( $2\theta$ ), recalling that the B-TC (pH 3) is the sample with the highest amount of TC adsorbed.

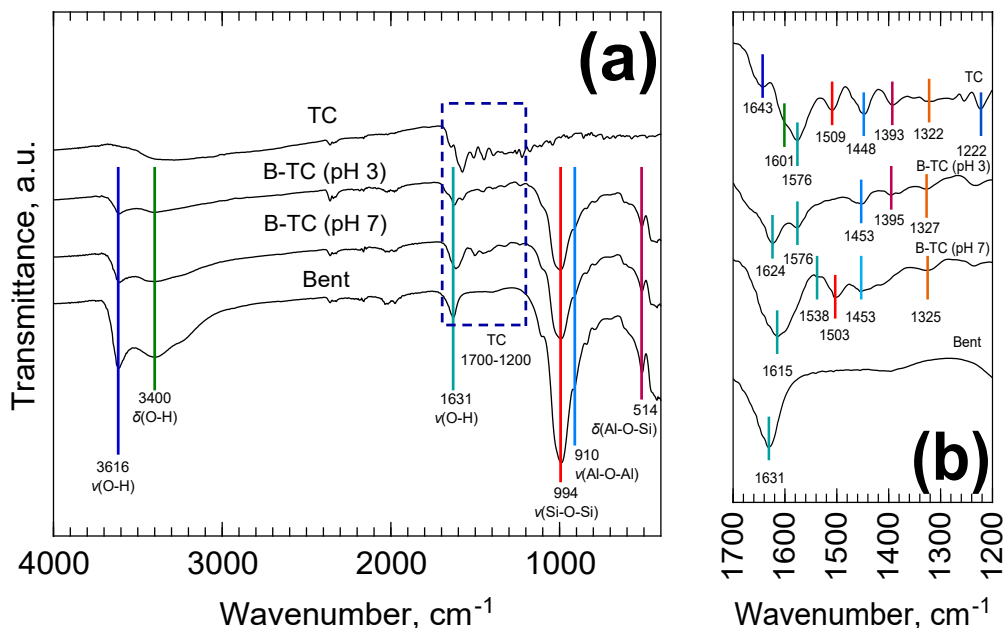


**Figure 4.7.** X-ray patterns obtained for Bent, B-TC (pH 3) and B-TC (pH 7) (a). Enlargement of the area depicting the (001) reflection of Bent (b).

#### 4.3.4 Infrared spectroscopy analysis

Figure 4.8 (a) displays the infrared spectra for Bent, B-TC (pH 3), B-TC (pH 7) and TC samples in the wavenumber range of  $400\text{--}4000\text{ cm}^{-1}$ . The spectrum of Bent shows an absorption band at  $514\text{ cm}^{-1}$  due to bending vibrations ( $\delta$ ) of the (Al-O-Si) bond, followed by a very strong band comprising the region between  $1071\text{--}900\text{ cm}^{-1}$ , corresponding to the stretching vibrations ( $\nu$ ) of the (Al-O-Al) and (Si-O-Si) bonds in Bent. The band at  $3616\text{ cm}^{-1}$  is associated with vibrations of the structural  $\nu(\text{OH})$  groups

of Bent, while the other around  $3400\text{ cm}^{-1}$  represents the -OH groups coordinated by hydrogen bonding  $\delta(\text{O-H})$ . Alabarse et al. (2011) found out that the  $\nu(\text{O-H})$  vibration of interlayer water is shown at  $1631\text{ cm}^{-1}$ .



**Figure 4.8.** FT-IR spectra of Bent, B-TC (pH 3), B-TC (pH 7) and TC (a). The amplification of the spectra selected by the blue dashed line showing the TC bands (b).

The absorption bands of the TC spectrum are at 1643, 1509 and  $1222\text{ cm}^{-1}$ , Figure 4.8 (b), and designated as Amides I, II and III, corresponding to vibrations of the bonds  $\nu(\text{C=O})$ ,  $\delta(\text{N-H})$  and  $\nu(\text{C-N})$  about the amide group. The vibrations of the  $\nu(\text{C=O})$  bond of the A and C rings (See Figure 4.1 (a)) are displayed at 1601 and  $1576\text{ cm}^{-1}$ , respectively. The band at  $1448\text{ cm}^{-1}$  matches to skeletal vibrations  $\nu(\text{C=C})$ , while those located between 1430 and  $1230\text{ cm}^{-1}$  are assigned to the  $\nu(\text{C-C})$ ,  $\delta(\text{C-C})$ ,  $\nu(\text{amine, N-H})$ ,  $\delta(\text{amine, C-N})$  and  $\nu(\text{C-O})$  bonds (Kang et al., 2011).

The TC bands in the B-TC (pH 3) and B-TC (pH 7) confirmed TC adsorption on Bent. The bands of the  $\delta(\text{C-N})$  ( $1393\text{ cm}^{-1}$ ) and  $\nu(\text{N-H})$  ( $1322\text{ cm}^{-1}$ ) bonds of the dimethylamino group shifted towards longer wavenumbers in B-TC (pH 3). Besides, the  $\nu(\text{O-H})$  band of interlaminar water showed a shift from  $1631$  to  $1624\text{ cm}^{-1}$ . This shift is related to the interaction between the group  $-\text{NH}(\text{CH}_3)_2^+$  ( $\text{TC}^+$  species) with the

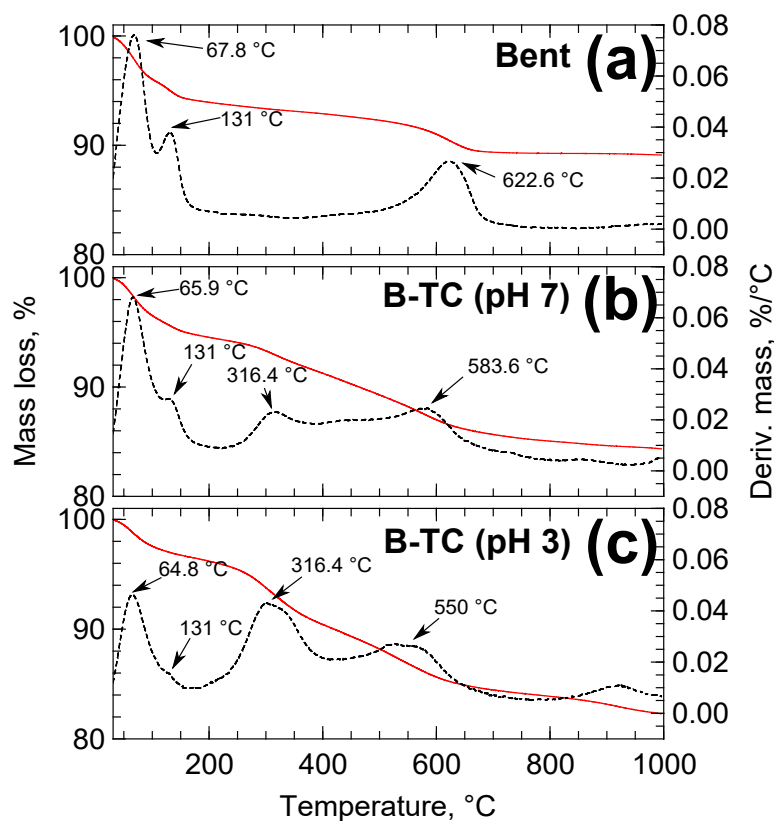
negative surface of Bent, and the coordination of the polar groups of  $\text{TC}^+$  with the hydration water of the clay by hydrogen bonds. B-TC (pH 7) showed a displacement of  $\nu(\text{N-H})$  band from 1322 to 1325  $\text{cm}^{-1}$  attributed to a weak electrostatic attraction between the  $-\text{NH}(\text{CH}_3)_2^+$  group ( $\text{TC}^\pm$  species) with the negative surface of Bent. Similarly, the  $\nu(\text{C=O})$  band of the C-ring of TC moved to lower wavenumbers (1538  $\text{cm}^{-1}$ ), and its intensity decreased also. This distortion can be related to the resonance of the double bond  $\text{C=O}$  of the C ring of the  $\text{TC}^-$  species with the oxygen bound in C12 (See Figure 4.1 (a)), causing a high electronic density that leads to a negative charge on the resonant ring. It has been reported that this negative charge is usually stabilized by the formation of coordination complexes with highly polarizable divalent cations (Lambs et al., 1988). The interlaminar water  $\nu(\text{O-H})$  band shifted from 1631 to 1615  $\text{cm}^{-1}$ , suggesting the formation of outer-sphere coordination complexes among the  $\text{TC}^-$  species and the hydration sphere of the interlaminar  $\text{Ca}^{2+}$  cation. These results agree with different adsorption studies of organic compounds on montmorillonite, which is the main component of Bent (Farmer and Mortland, 1966; Lu et al., 2010; Parfitt and Mortland, 1968; Yariv et al., 1966).

#### 4.3.5 Thermogravimetric analysis

The thermogravimetric analysis (TGA/DTG) of Bent, B-TC (pH 3) and B-TC (pH 7) samples are presented in Figure 4.9. The TGA curve of Bent, Figure 4.9 (a), displays a mass loss of around 6.1% from 25 to 200°C, associated with the water adsorbed onto the external surface and in the interlayer space of Bent. Subsequently, another mass loss of approximately 4.8% is observed between 200 and 1000°C, corresponding to dehydroxylation reactions in the octahedral sheet of Bent (Guggenheim and Koster van Groos, 2001). The overall mass loss from 25 to 1000°C was 10.9%, confirming the high thermal stability of Bent.

The TGA curves of B-TC (pH 7) and B-TC (pH 3) are shown in Figures 4.9 (b) and 4.9 (c), respectively, and a mass loss of 5.5% for B-TC (pH 7) and 3.8% for B-TC (pH 3) is observed between 25 and 200°C associated to the water adsorbed on the B-TC. In the range 200-1000°C, a mass loss of 10.2 and 13.9% is noticed for B-TC (pH

7) and B-TC (pH 3), respectively, confirming the decomposition of the TC adsorbed and dehydroxylation reactions (Cervini et al., 2016). The TC decomposition in both samples mainly occurred at 316.4°C. Assuming that the mass loss caused by dehydroxylation of the structural -OH groups of Bent (4.8%) is the same as those for B-TC (pH 7) and B-TC (pH 3); thus, the decomposition of the TC was 5.4 and 9.1%, respectively. The mass adsorbed of TC on B-TC (pH 7) and B-TC (pH 3) was  $q = 153.3$  and  $257.2$  mg/g, respectively, then only 37.1 and 38.9% of the mass of TC adsorbed was decomposed in B-TC (pH 7) and B-TC (pH 3). This finding reveals that the TC adsorbed did not completely decompose in the temperature range used in this work. The partial decomposition of TC adsorbed is explained, recalling that part of TC intercalated in Bent interlayer space and Bent structure protected TC molecules thermally.



**Figure 4.9.** TGA (red line) and DTG (black dashed line) curves obtained for Bent (a), B-TC (pH 7) (b) and B-TC (pH 3) (c).

### 4.3.6 Adsorption isotherms of TC

The experimental data for the TC adsorption equilibrium onto raw clays were interpreted using the Radke-Prausnitz (R-P), Freundlich and Langmuir mathematical models expressed by the succeeding equations:

$$q = kC_e^{1/n} \quad (4.9)$$

$$q = \frac{q_m KC_e}{1 + KC_e} \quad (4.10)$$

$$q = \frac{aC_e}{1 + bC_e^\beta} \quad (4.11)$$

where  $k$  ( $\text{mg}^{1-1/n} \text{ L}^{1/n}/\text{g}$ ) is a parameter associated with adsorption capacity,  $q_m$  ( $\text{mg/g}$ ) represents the maximum mass of TC adsorbed,  $K$  ( $\text{L/mg}$ ) is a parameter associated with the heat of adsorption, and  $a$  ( $\text{L/g}$ ),  $b$  ( $\text{L}^\beta/\text{mg}^\beta$ ) and  $\beta$  are constants of the R-P isotherm.

Table 4.3 lists the average percentage deviations (%D) and the parameters for each isotherm. The parameters were assessed employing a nonlinear least-squares optimization procedure and the Rosenbrock-Newton algorithm, and %D was appraised with the succeeding relationship:

$$\%D = \left( \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{i,\text{exp}} - q_{i,\text{pred}}}{q_{i,\text{exp}}} \right| \right) \times 100 \% \quad (4.12)$$

where  $N$  is the number of experimental data points;  $q_{i,\text{exp}}$  is the uptake adsorbed of TC evaluated experimentally,  $\text{mg/g}$ ;  $q_{i,\text{pred}}$  is the uptake adsorbed of TC computed using the adsorption isotherm,  $\text{mg/g}$ .

In 12 out of 15 cases of the experimental conditions presented in Table 4.3, the %D obtained for the Langmuir and R-P isotherms were smaller than those for the Freundlich model. Besides, 9 out of 15 cases, the parameter  $\beta$  of the R-P model is  $\beta = 1$ , so the R-P isotherm transforms into the Langmuir isotherm model. For this reason, Langmuir isotherm was chosen for predicting the experimental data.

**Table 4.3.** Adsorption isotherm parameters and average percentage deviation for the adsorption of TC on raw clays.

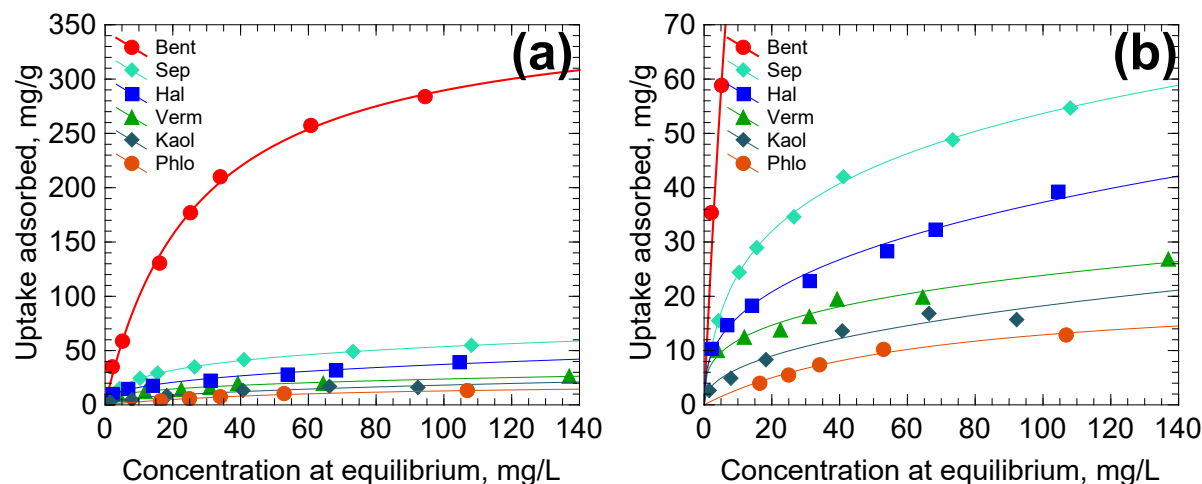
| Natural clays | pH | I (N) | T (°C) | Freundlich                                        |      |      | Langmuir     |          |      | Radke-Prausnitz |                                |         |      |
|---------------|----|-------|--------|---------------------------------------------------|------|------|--------------|----------|------|-----------------|--------------------------------|---------|------|
|               |    |       |        | K ( $\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$ ) | n    | %D   | $q_m$ (mg/g) | K (L/mg) | %D   | a (L/g)         | b ( $\text{L}^b/\text{mg}^b$ ) | $\beta$ | %D   |
| Sep           | 3  | 0.01  | 25     | 10.75                                             | 2.83 | 3.8  | 60.53        | 0.061    | 6.0  | 8.30            | 0.418                          | 0.77    | 0.9  |
| Verm          | 3  | 0.01  | 25     | 5.93                                              | 3.31 | 5.7  | 26.45        | 0.069    | 13.9 | 8.23            | 0.980                          | 0.78    | 7.0  |
| Phlo          | 3  | 0.01  | 25     | 0.97                                              | 1.78 | 9.5  | 21.33        | 0.015    | 5.4  | 0.33            | 0.015                          | 1.00    | 5.4  |
| Hal           | 3  | 0.01  | 25     | 7.00                                              | 2.75 | 4.7  | 39.56        | 0.068    | 16.0 | 46.91           | 6.239                          | 0.65    | 5.3  |
| Kaol          | 3  | 0.01  | 25     | 2.42                                              | 2.28 | 10.6 | 21.26        | 0.041    | 13.9 | 1.59            | 0.249                          | 0.75    | 13.3 |
| Bent          | 3  | 0.01  | 25     | 36.15                                             | 2.14 | 16.0 | 367.50       | 0.037    | 4.2  | 13.00           | 0.035                          | 1.00    | 5.0  |
|               | 5  | 0.01  | 25     | 30.28                                             | 2.12 | 20.3 | 334.52       | 0.032    | 10.7 | 10.81           | 0.034                          | 0.99    | 10.7 |
|               | 7  | 0.01  | 25     | 22.83                                             | 2.14 | 14.5 | 243.70       | 0.034    | 4.2  | 7.03            | 0.027                          | 1.00    | 4.2  |
|               | 3  | 0.05  | 25     | 40.35                                             | 2.38 | 20.0 | 344.31       | 0.038    | 3.5  | 12.98           | 0.038                          | 1.00    | 3.5  |
|               | 3  | 0.10  | 25     | 35.58                                             | 2.31 | 21.9 | 340.07       | 0.032    | 7.3  | 11.13           | 0.033                          | 1.00    | 7.5  |
|               | 3  | 0.50  | 25     | 9.38                                              | 1.44 | 8.9  | 428.14       | 0.011    | 3.4  | 4.51            | 0.011                          | 1.00    | 3.5  |
|               | 7  | 0.05  | 25     | 18.10                                             | 1.87 | 17.5 | 290.56       | 0.023    | 8.8  | 7.07            | 0.025                          | 1.00    | 9.3  |
|               | 7  | 0.10  | 25     | 17.30                                             | 1.91 | 18.1 | 264.81       | 0.023    | 9.8  | 6.21            | 0.023                          | 1.00    | 9.8  |
|               | 7  | 0.01  | 15     | 17.94                                             | 2.07 | 5.6  | 230.01       | 0.025    | 6.5  | 11.69           | 0.244                          | 0.70    | 3.5  |
|               | 7  | 0.01  | 35     | 21.33                                             | 1.87 | 18.3 | 317.34       | 0.027    | 9.2  | 8.61            | 0.027                          | 1.00    | 9.2  |

#### 4.3.7 Comparing the adsorption capacity of TC on various raw clays

At pH = 3 and T = 25°C, the adsorption isotherms of TC onto Sep, Bent, Phlo, Hal, Verm and Kaol are displayed in Figure 4.10 (a). Also, Figure 4.10 (b) shows an amplification of the adsorption isotherms in the uptake of TC adsorbed range from 0 to 70 mg/g. The experiments were performed at pH = 3 to favor the adsorption on acidic clays because the predominant species of TC was the cationic species ( $\text{TC}^+$ ) in the water solution. The results showed that Bent exhibited the maximum mass adsorbed of TC, 283.5 mg/g, and the capacities diminished as follows: Bent >> Sep > Hal > Verm > Kaol  $\approx$  Phlo. For a TC equilibrium concentration of 100 mg/L, the Bent adsorption capacity towards TC was 5.40-fold higher than that for Sep and up to 22.5-fold larger than that for Phlo.

The highest capacity of Bent for adsorbing TC can be related to their structural arrangement, the swelling capacity, the degree of isomorphous substitution, and the residual charges in its structure. Verm and Phlo have a similar laminar structure like Bent; however, the  $\text{Mg}^{2+}$  and  $\text{K}^+$  ions are the main interlayer cations in these clays

(Domínguez and Schifter, 1992). These cations promote higher residual charges, generating strong bonds between the interlaminar ions and the clay sheets, diminishing the adsorption of TC. Even though Kaol is considered a swelling clay, it presented low TC adsorption capacity due to the large molecular size of TC. On the other hand, Sep and Hal cannot swell because of their fibrous and tubular structures, hindering that the molecules of TC can access the Sep channels or the interior of the Hal tubular structure.



**Figure 4.10.** Effect of the type of raw clay on the adsorption isotherms of TC at pH = 3 and T = 25 °C (a). Amplification in the uptake of TC adsorbed range from 0 to 70 mg/g (b). The lines represent the best-fit isotherm.

Table 4.4 shows the TC mass adsorbed on different materials, and the Bent used in this work presented a maximum mass adsorbed of 283.5 mg/g, which is larger than the capacities found for other raw clays and even comparable or superior to carbon-based adsorbents. Furthermore, Bent presents outstanding advantages such as low cost and abundance, making Bent a very effective adsorbent for eliminating TC from aqueous solutions.

#### 4.3.8 Influence of solution pH upon the capacity of bentonite for adsorbing TC

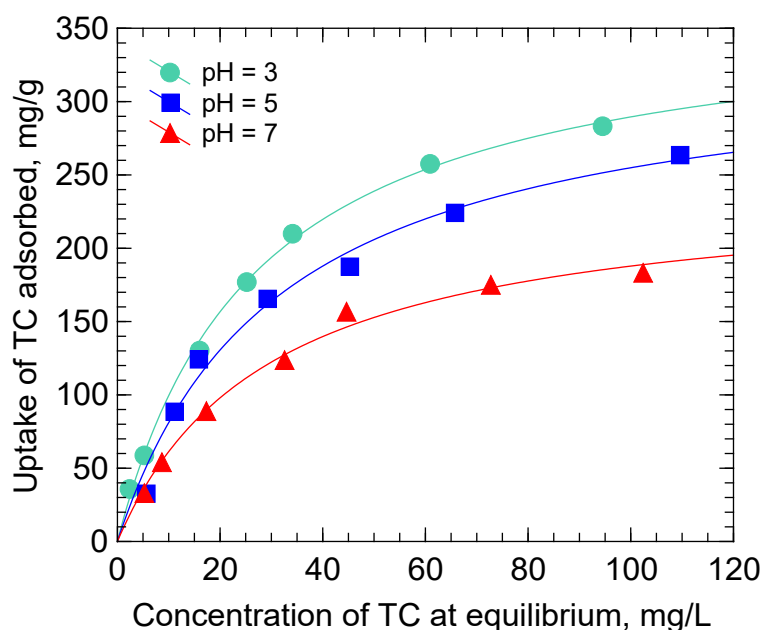
Figure 4.11 depicts the solution pH effect upon the TC adsorption onto Bent at 25 °C and pH of 3, 5 and 7. No adsorption runs were carried out at pH > 7 since it was observed that TC was partially mineralized in alkaline media. The maximum adsorption

capacity was 183.1, 263.8 and 283.5 mg/g for pH of 7, 5, and 3, correspondingly, so that the capacity for adsorbing TC notably diminishes by incrementing pH, and the highest uptake of TC adsorbed was at pH = 3. According to the results, the affinity of Bent towards the species of TC decreases as follows:  $TC^+ > TC^\pm > TC^-$ . At pH = 3,  $TC^+$  is the predominant species, and Bent surface is negative so that the adsorption capacity is favored by electrostatic attractions among  $TC^+$  and the negative surface charge of Bent. Moreover, the contribution of electrostatic attraction to the adsorption of  $TC^\pm$  and  $TC^-$  on Bent is not significant at pH = 7 because the net charge of these species is 0 and -1, respectively, and the Bent surface is negatively charged. Hence, the species  $TC^\pm$  and  $TCH^-$  would not be attracted or repelled from the surface of the clay, suggesting that the adsorption of both species on Bent is mainly due to other mechanisms.

**Table 4.4.** Adsorption capacities of several adsorbent materials towards TC.

| Adsorbents                             | Maximum<br>adsorption capacity<br>(mg/g) | Experimental<br>conditions | Reference                    |
|----------------------------------------|------------------------------------------|----------------------------|------------------------------|
| Commercial<br>activated carbon         | 471.1                                    | pH = 7-8, T = 25°C         | Rivera-Utrilla et al. (2013) |
| Granular activated<br>carbon           | 375.4                                    | pH = 7-8, T = 25°C         | Rivera-Utrilla et al. (2013) |
| Graphene oxide                         | 313.0                                    | pH = 3.6, T = 25°C         | Gao et al. (2012)            |
| <b>Bentonite</b>                       | <b>283.5</b>                             | <b>pH = 3, T = 25°C</b>    | <b>This work</b>             |
| Montmorillonite                        | 250.0                                    | pH = 5.5, T = 25°C         | Zhao et al. (2012)           |
| MOF graphite oxide<br>pellets          | 228.0                                    | pH = 4, T = 25°C           | Yu et al. (2018)             |
| Rectorite                              | 140.0                                    | pH = 4-5, T = 25°C         | Chang et al. (2009)          |
| Multi-walled carbon<br>nanotubes       | 100.0                                    | pH = 5.8, T = 25°C         | Ji et al. (2009)             |
| Nano sheet layered<br>double hydroxide | 98.04                                    | pH = 3, T = 10°C           | Soori et al. (2016)          |
| Illite                                 | 32.0                                     | pH = 5-6, T = 25°C         | Chang et al. (2012)          |





**Figure 4.11.** Effect of the solution pH on the adsorption isotherms of TC on Bent at  $T = 25\text{ }^{\circ}\text{C}$ . The lines represent the Langmuir isotherm.

#### 4.3.9 Analysis of cations exchanged during adsorption of TC

This analysis was performed by a two-step procedure described above. The amount of each exchangeable cation ( $Q_i$ ) and  $\text{H}^+$  ( $Q_{\text{H}^+}$ ) adsorbed or desorbed on the clay during the TC adsorption on Bent at pH 3 and 7 are given in Table 4.5. At pH = 3, the  $Q_i$  values were negative, indicating that the exchangeable cations were desorbed from the Bent to the solution, and the opposite occurred with the  $\text{H}^+$ . Li et al. (2010) noted similar trends for the adsorption of TC on smectite. At pH = 3, the  $\text{TC}^+$  and  $\text{H}^+$  competed for the same adsorption sites, and this tendency was found by Zhao et al. (2012) for the TC adsorption onto montmorillonite. The total uptake of exchangeable cations and  $\text{H}^+$ ,  $Q_{\text{T,Cat}}$ , was  $-57.39\text{ cmol}(+)/\text{kg}$ , almost the same as the uptake of TC,  $Q_{\text{TC}}$ , of  $57.9\text{ cmol}(+)/\text{kg}$ , which is lower than the CEC of Bent ( $75.2\text{ cmol}(+)/\text{kg}$ ). Thus, the adsorption of  $\text{TC}^+$  and  $\text{H}^+$  on TC was essentially due to the cation exchange of the exchangeable cations. Wang et al. (2010) reported similar results for the ciprofloxacin adsorption on montmorillonite.

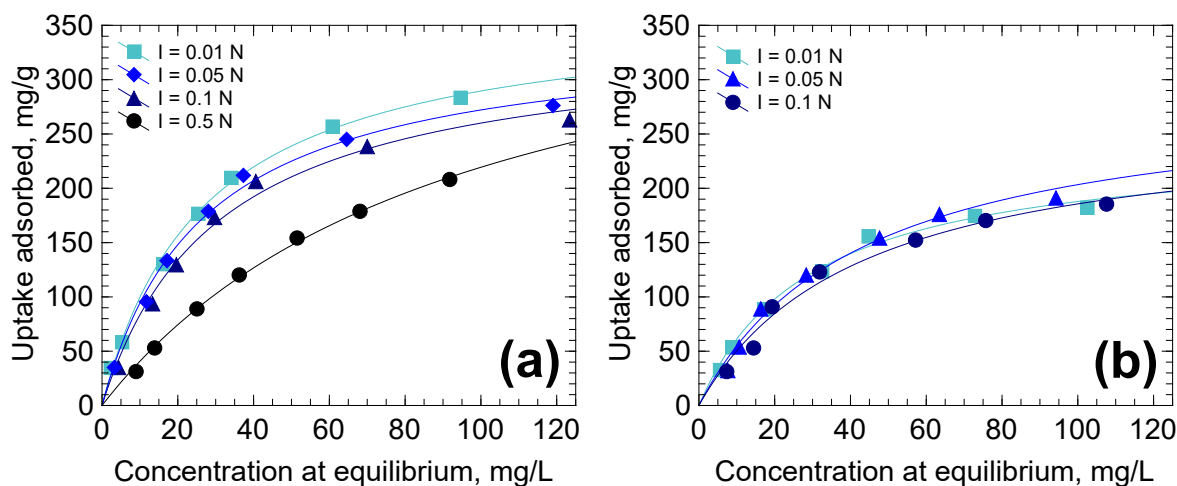
**Table 4.5.** Exchangeable cations and  $H^+$  concentration at the beginning and the end of the adsorption of TC on Bent and uptake of TC adsorbed on Bent.

| Species     | B-TC (pH = 3)                             |                                |                         | B-TC (pH = 7)                              |                                |                         |
|-------------|-------------------------------------------|--------------------------------|-------------------------|--------------------------------------------|--------------------------------|-------------------------|
|             | $Q_{TC} = 57.9 \text{ cmol(+)}/\text{kg}$ |                                |                         | $Q_{TC} = 35.18 \text{ cmol(+)}/\text{kg}$ |                                |                         |
|             | $C_{i0} \times 10^5$<br>(eq/L)            | $C_{if} \times 10^5$<br>(eq/L) | $Q_i$<br>(cmol(+) / kg) | $C_{i0} \times 10^5$<br>(eq/L)             | $C_{if} \times 10^5$<br>(eq/L) | $Q_i$<br>(cmol(+) / kg) |
| $Mg^{2+}$   | 9.93                                      | 13.98                          | -5.35                   | 6.87                                       | 1.07                           | 4.66                    |
| $Ca^{2+}$   | 25.15                                     | 41.77                          | -21.93                  | 16.99                                      | 4.89                           | 9.72                    |
| $K^+$       | 8.12                                      | 12.10                          | -5.25                   | 8.52                                       | 6.04                           | 2.00                    |
| $Na^+$      | 937.9                                     | 1025                           | -115.1                  | 934.9                                      | 1013.9                         | -63.41                  |
| $H^+$       | 100                                       | 31.62                          | 90.27                   | 0.010                                      | 0.012                          | -0.0025                 |
| $Q_{T,Cat}$ |                                           |                                | -57.39                  |                                            |                                | -47.03                  |
| TC          | 57.50                                     | 13.7                           |                         | 53.90                                      | 10.1                           |                         |

At pH = 7, the uptakes of the  $Mg^{2+}$ ,  $Ca^{2+}$  and  $K^+$  cations were positive, confirming that these cations were adsorbed on the surface of Bent. In contrast, the uptakes of  $Na^+$  and  $H^+$  ( $Q_{H^+}$ ) were negative, showing that both cations were desorbed from the Bent surface; however,  $Q_{H^+}$  was insignificant. The value of  $Q_{T,Cat}$  was -47.03 cmol(+) / kg, while the uptake of TC adsorbed was 35.18 cmol(+) / kg. According to the speciation diagram (Figure 4.1 (b)), at pH = 7, the species of TC present in water solution were the anionic species  $TC^-$  (16.6%) and the zwitterionic species  $TC^\pm$  (83.6%), but the cationic group  $-NH(CH_3)_2^+$  of  $TC^-$  and  $TC^\pm$  can interact with the negatively charged Bent surface (Parolo et al., 2013). Furthermore, at pH > 6, the species of TC present in the solution can be affected by the concentration of  $Mg^{2+}$  and  $Ca^{2+}$ . The reduction of the  $Mg^{2+}$  and  $Ca^{2+}$  concentrations in the solution can also be ascribed to forming outer-sphere coordination complexes between the  $TC^-$  and  $Ca^{2+}$  and  $Mg^{2+}$  such as  $Ca(TCH)_2$  and  $CaTC(TCH)^-$  (Lambs et al., 1988; Parolo et al., 2013). Other works have described the occurrence of these complexes in the adsorbing mechanism of TC on montmorillonite (Parolo et al., 2013; Zhao et al., 2012).

#### 4.3.10 Variation of the adsorption capacity of bentonite with the ionic strength

The importance of the solution ionic strength (0.01, 0.05, and 0.1 N) in the adsorption of TC on Bent at pH = 7 and 3 and 25°C is illustrated in Figure 4.12. As noticed in Figure 4.12 (a), the mass of TC adsorbed diminishes by incrementing the solution ionic strength. Incrementing the ionic strength from 0.01 to 0.1 N resulted in an 11.4% reduction of the uptake of TC adsorbed at an equilibrium concentration of 60 mg/L. Additional experiments at a higher ionic strength of 0.5 N revealed that the adsorption diminished 34.74% from 0.01 N to 0.5 N. At pH = 7, the mass of TC adsorbed did not show a significant change by rising the solution ionic strength (See Figure 4.12 (b)).



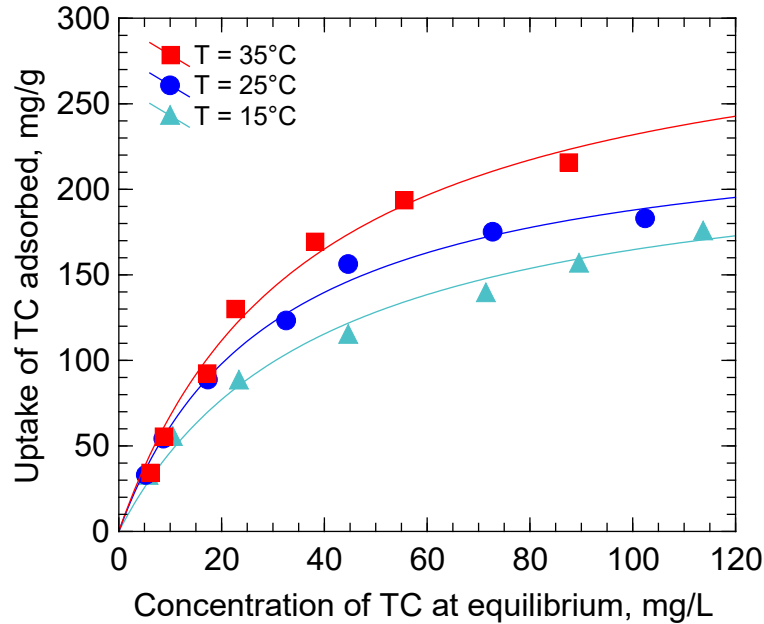
**Figure 4.12.** Effect of the solution ionic strength on the adsorption isotherms of TC on Bent at T = 25 °C and pH = 3 (a) and pH = 7 (b). The lines represent the Langmuir isotherm.

These studies showed a competition among the TC<sup>+</sup> species and Na<sup>+</sup> ions in solution for the available adsorption sites and further confirmed that electrostatic attractions and cation exchange have an essential role in the uptake of adsorbed of TC on Bent at pH = 3. There is no crucial decrease in the mass adsorbed at lower ionic strength since the concentration of Na<sup>+</sup> cations cannot compete significantly for adsorption sites. In contrast, at a higher Na<sup>+</sup> concentration, the TC adsorption diminishes. At pH = 7, the Bent adsorption capacity does not depend on the

concentration of  $\text{Na}^+$  ions, confirming the presence of weak electrostatic interactions in the adsorption mechanism of the  $\text{TC}^\pm$  species.

#### 4.3.11 Variation of the bentonite adsorption capacity with temperature

The influence of temperature upon the capacity of Bent for adsorbing TC is presented in Figure 4.13. The Bent adsorption capacity towards TC raises incrementing the temperature; for an equilibrium concentration of 100 mg/L, the uptake adsorbed of TC was 231.8, 187.8, and 164.7 mg/g at 35, 25, and 15 °C, sequentially, indicating a decrease in adsorption capacity of about 1.40 times, while the temperature reduces from 35 to 15°C.



**Figure 4.13.** Effect of the temperature on the adsorption isotherms of TC on Bent at pH = 7. The lines represent the Langmuir isotherm.

The isosteric heat of adsorption was appraised with the succeeding relationship:

$$(\Delta H_{\text{ads}})_q = \frac{R \ln \left( \frac{C_{e1}}{C_{e2}} \right)}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (4.13)$$

where  $C_{e1}$  and  $C_{e2}$  denote the concentrations of TC at the temperatures  $T_1$  and  $T_2$ , correspondingly, both at the same mass of TC adsorbed, mg/L;  $T$  is the solution temperature, K;  $R$  is the ideal gas constant, 8.314 J/mol K;  $(\Delta H_{ads})_q$  stands for the isosteric heat of adsorption of TC onto Bent for a given mass of TC adsorbed, J/mol.

For a mass of TC adsorbed of 172.8 mg/g, the TC equilibrium concentrations were  $C_{e1} = 38.2$  mg/L ( $T_1 = 308.15$  K) and  $C_{e2} = 113.4$  mg/L ( $T_2 = 288.15$  K). The  $(\Delta H_{ads})_q$  was 40.3 kJ/mol, indicating that TC adsorption on Bent is endothermic. Chemical adsorption is characterized by having high heat of adsorption similar to those for chemical reactions ( $> 40$  kJ/mol) (Leyva-Ramos, 2010). The results demonstrate that adsorption of TC on Bent at pH = 7 occurs by physical and chemical interactions.

#### 4.3.12 Desorption of TC adsorbed on bentonite

The reversibility of TC adsorbed on Bent was analyzed by conducting adsorption runs at pH = 3 and subsequently desorbing at pH = 3 and 7. At pH = 3, the experimental data for adsorption equilibrium data are shown in Figure 4.14, denoted by the letter A and followed by the experiment number. Likewise, the experimental data for desorption equilibrium are represented as D3 and D7, where 3 and 7 are related to the desorption pH and preceded by the desorption experiment number.

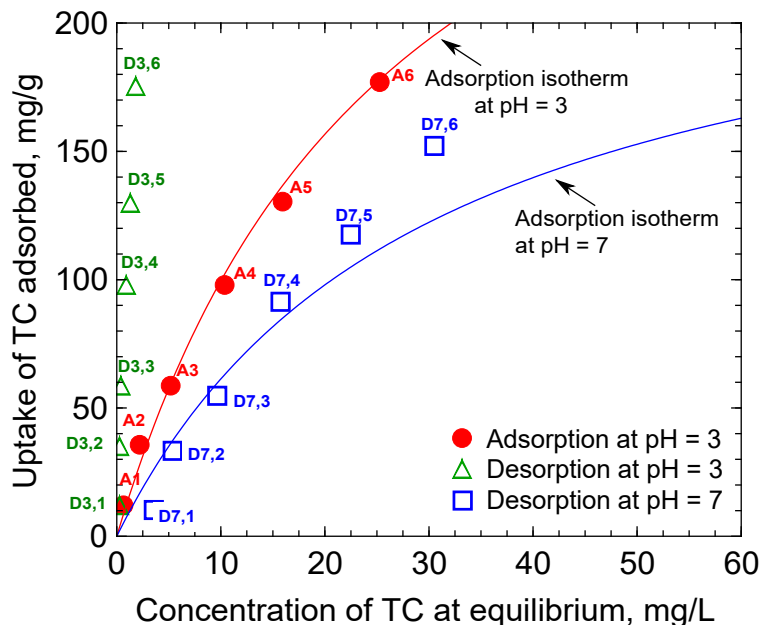
The adsorption process could be considered reversible when the desorption equilibrium data were on the adsorption isotherm. As shown in Figure 4.14, the desorption equilibrium data for pH = 3 is over the adsorption isotherm at pH = 3. On the other hand, the desorption equilibrium data for pH = 7 were relatively close to the adsorption isotherm (pH of 7).

The desorption percentage, %Des, was computed from the succeeding equation:

$$\%Des = \frac{q_o - q_d}{q_o - q_{d,rev}} \times 100 \% \quad (4.14)$$

where  $q_o$  and  $q_{ed}$  are the uptakes of TC adsorbed at the start, and the termination of the desorption experiment and the uptake of TC adsorbed at the desorption equilibrium supposing that the adsorption is reversible is denoted as  $q_{d,rev}$ . The adsorption could

be considered reversible if the %Des was equal to 100%. Contrarily, the adsorption would be irreversible when %Des was less than 100%. The  $q_{d,rev}$  was computed by solving the Langmuir isotherm and Equation (4.3) representing the desorption mass balance.



**Figure 4.14.** Adsorption isotherm of TC on Bent at pH = 3 and T = 25 °C; and desorption isotherm of TC at pH of 3 and 7. The lines represent the Langmuir isotherm.

Table 4.6 lists the  $q_o$ ,  $q_d$ ,  $q_{d,rev}$  and %Des, and the %Des values vary from 72.0 to 100% and 8.50 to 27.4% for pH of 7 and 3, respectively. At pH = 3, the average %Des was 11.99%, revealing that the adsorption was essentially irreversible and mainly due to chemical adsorption. Moreover, at pH = 7, the adsorption was reversible for concentrations at equilibrium lower than 10 mg/L because the %Des values were very close to 100%. Nevertheless, for concentrations bigger than 10 mg/L, %Des varied between 70 and 90%, indicating that desorption was irreversible. The partial desorption of the TC by raising the solution pH corroborated that the chemical and physical mechanisms were involved in the TC adsorption at pH = 7.

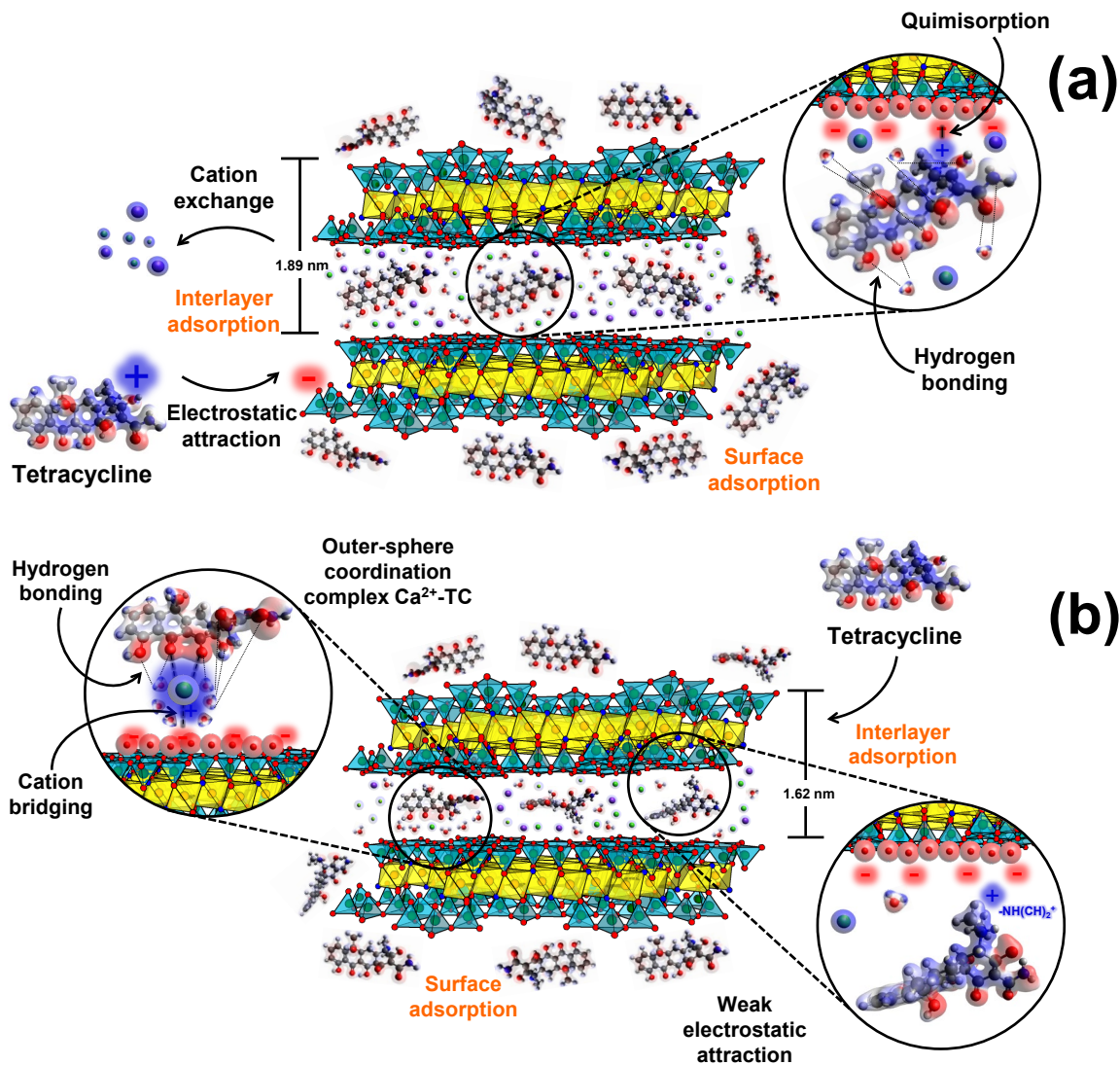
**Table 4.6.** Desorption percentages of TC from Bent at T = 25 °C.

| Exp. No. | q <sub>0</sub><br>(mg/g) | Desorption at pH = 7     |                              |        | Desorption at pH = 3     |                              |      |
|----------|--------------------------|--------------------------|------------------------------|--------|--------------------------|------------------------------|------|
|          |                          | q <sub>d</sub><br>(mg/g) | q <sub>d,rev</sub><br>(mg/g) | %Des   | q <sub>d</sub><br>(mg/g) | q <sub>d,rev</sub><br>(mg/g) | %Des |
| 1        | 11.98                    | 10.57                    | 11.39                        | ~100.0 | 11.88                    | 11.62                        | 27.4 |
| 2        | 35.44                    | 33.35                    | 33.56                        | ~100.0 | 35.33                    | 34.64                        | 10.0 |
| 3        | 58.78                    | 55.10                    | 55.34                        | ~100.0 | 58.64                    | 56.84                        | 7.1  |
| 4        | 98.11                    | 91.86                    | 91.02                        | 88.1   | 97.75                    | 94.39                        | 9.7  |
| 5        | 130.6                    | 117.8                    | 115.3                        | 84.0   | 129.9                    | 122.9                        | 9.3  |
| 6        | 176.97                   | 152.64                   | 143.2                        | 72.0   | 175.56                   | 160.3                        | 8.5  |

#### 4.3.13 Adsorption mechanisms of TC on bentonite

The adsorption of TC on Bent depends on the solution pH because of the changes experienced by the chemical groups of the TC molecule and the surface charge of Bent. At pH = 3, where the TC<sup>+</sup> species predominates, adsorption occurs onto Bent external surface and in the interlaminar space, and it is governed by electrostatic attractions, followed by the cationic exchange between interlaminar cations, particularly Ca<sup>2+</sup>, and the TC<sup>+</sup> species (Figure 4.15 (a)). Also, there is interaction through hydrogen bonding between the polar groups of the adsorbed TC molecule and the hydrated water of the exchangeable cations, which were not released from the interlayer space of Bent. At pH = 7, the coexisting species TC<sup>±</sup> and TC<sup>-</sup> can be adsorbed by physical and chemical mechanisms. In the first mechanism, adsorption occurs onto the Bent external surface and in the interlaminar space and is promoted by weak physical interactions between the -NH(CH<sub>3</sub>)<sub>2</sub><sup>+</sup> group of the TC<sup>±</sup> species and the negative charge of Bent. Herein, TC<sup>±</sup> orients as closely as possible to the cationic sites of Bent. The second mechanism involves forming outer-sphere coordination complexes between the TC<sup>-</sup> species and the internal sphere of hydration of the interlaminar Ca<sup>2+</sup> ion. At this point, the ionization of the phenolic-diketone group causes a high electron density, allowing that the positive charge of the Ca<sup>2+</sup> ions can be partially shared with the anionic TC<sup>-</sup> species. Through electronic delocalization on the chelating ring, the coordination complex stabilizes the electronic density, avoiding the repulsive forces and

allowing the adsorption via forming cationic bonding between the TC<sup>-</sup> species and the cationic sites of Bent Figure 4.15 (b).



**Figure 4.15.** Adsorption mechanisms of TC on Bent at pH = 3 (a) and pH = 7 (b).

#### 4.4 Conclusions

The capacity of the raw clays for adsorbing TC from water is strongly influenced by its structural arrangement, swelling capability, nature of interlayer cations, and the TC molecular size. Bent showed the highest adsorption capacity, while the uptakes of TC adsorbed on Sep, Hal, Verm, Kaol, and Phlo fluctuated from 10 to 60 mg/g. The



uptake of TC adsorbed on Bent was significantly influenced by the solution pH. At  $T = 25^{\circ}\text{C}$  and pH of 3, the maximum mass adsorbed of TC was 283.5 mg/g, where  $\text{TC}^+$  is the dominant species. The effect of the ionic strength revealed the presence of electrostatic and non-electrostatic mechanisms. The TC adsorption on Bent is endothermic, and the desorption of TC is partially reversible, proving that physical and chemical mechanisms can explain the TC adsorption.

The characterization of TC adsorbed on Bent revealed that adsorption occurred onto both the external surface and in the interlayer space of Bent. At  $\text{pH} = 3$ , the adsorption of  $\text{TC}^+$  is governed by cation exchange and electrostatic attractions, and basal space (001) was 1.89 nm, indicating a parallel and inclined orientation of the  $\text{TC}^+$  species in the interlayer space. Otherwise, at  $\text{pH} = 7$ , the adsorption of  $\text{TC}^{\pm}$  species was carried out by weak electrostatic attractions, whereas the  $\text{TC}^-$  species was adsorbed by outer-sphere coordination complexes of the type  $\text{Ca}^{2+}\text{-TC}$ . Likewise, the basal reflection (001) was 1.62 nm, confirming the partial intercalation of the  $\text{TC}^{\pm}$  and  $\text{TC}^-$  species within the interlaminar space of Bent.

# CHAPTER

# 5

**IMPACT OF CHEMICAL,  
TEXTURAL AND SWELLING  
PROPERTIES OF BENTONITE  
CLAY ON ITS ADSORPTION  
CAPACITY FOR TRIMETHOPRIM  
AND CHLORPHENAMINE IN  
AQUEOUS SOLUTIONS**

## **5.1 Introduction**

The rapid growth of the world population and the increase in human activities have led to the emergence of numerous contaminants in water sources, including surface water, groundwater, drinking water, and wastewater treatment plant effluents. Among the various pollutants, pharmaceutical compounds stand out as they are found in alarming concentrations in these water sources (Ahuja, 2021).

Trimethoprim (TMP) is a highly effective bacteriostatic antibiotic commonly used to treat a variety of infections, including those of the intestinal, urinary, and respiratory tracts, as well as other diseases such as enterocolitis, otitis, and bronchitis (Barry and Pattishall, 1983; Brogden et al., 1982). On the other hand, chlorphenamine (CPA) is a first-generation antihistamine used to prevent and treat respiratory and skin infections, such as allergic rhinitis, colds, and urticaria (Rumore, 1984). Due to their widespread use, TMP and CPA have been detected in surface waters at concentrations ranging from 0.5 to 27.43 ng/L, and in effluents from wastewater treatment plants at levels varying from 4.9 to 788 ng/L (Biel-Maeso et al., 2018; Chernova et al., 2021; Guruge et al., 2019; Letsinger and Kay, 2019; Roberts et al., 2016; P. Zhang et al., 2018).

The physical and chemical properties of pharmaceutical compounds hinder the efficiency of conventional water treatment methods such as coagulation, filtration, flocculation, and biological processes, which are generally designed for more stable and common pollutants. Prominent methods include UV/Cl<sub>2</sub> processes for TMP removal by simultaneous chlorine and UV irradiation (Teo et al., 2022), as well as the heterogeneous photocatalysis using graphene oxide-coated Cu/Fe layered double hydroxide (CuFe-LDH/GO) activated with persulfate for TMP photodegradation (Vasseghian et al., 2023). In addition, photocatalytic degradation of CPA with iron-doped silica xerogels (XGS-Fe) (García-Reyes et al., 2022) and graphene oxide and magnetite nanocomposites (GO-Fe<sub>3</sub>O<sub>4</sub>) under sunlight irradiation has been explored (Chen et al., 2020). However, it is important to highlight that complete removal of TMP, CPA and other pharmaceuticals via these alternative processes was not achieved, and their degradation is partial under acidic and alkaline conditions. Furthermore, the

presence of carcinogenic nitrosamines byproducts detected in these disinfection processes raises significant health and environmental concerns.

For decades, adsorption on carbon-based materials has been effective in removing various pharmaceuticals, including TMP and CPA. Adsorption process offers advantages, including lower initial costs, simple design, ease of use, and the absence of hazardous byproducts (Rathi and Kumar, 2021). Carrales-Alvarado et al. (2020) studied the adsorption of TMP on graphene oxide and graphite materials with different physicochemical properties and surface areas. They found that the adsorption capacity increased with surface area due to  $\pi$ - $\pi$  dispersive interactions, and the graphene oxide exhibited the highest uptake of TMP (210 mg/g) at pH 10. In another study, the adsorption of CPA was performed using activated carbon (AC) from palm leaves, subjected to KOH activation and HNO<sub>3</sub> oxidation to obtain and oxidized activated carbon (OAC). Besides, this OAC was functionalized with ethylenediamine to produce a basic surface (BAC-EDA) and then with ethylamine to generate a hydrophobic carbonaceous surface (HAC-EA). The results showed that HAC-EA had the highest adsorption capacity (490 mg/g) at pH 7 and 35 °C. The uptake of CPA adsorbed diminishes in the following order: HAC-EA > OAC > AC > BAC-EDA (Ali et al., 2019).

Clays are natural adsorbents with unique chemical, structural, and swelling properties. Among its outstanding characteristics, the specific surface area and the cation exchange capacity stand out. Bentonite, a well-known clay, is rich in montmorillonite phase and belongs to the smectite group; its 2:1 layered structure consists of an octahedral layer of Al<sup>3+</sup> sandwiched between two tetrahedral layers of Si<sup>4+</sup>. The chemical peculiarity of bentonite lies in the fact that the central cations of its structure can be replaced by lower-charged atoms, creating an excess of negative charge on its surface. To balance this negative charge, bentonite contains interlaminar cations such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>.

In the field of TMP and CPA adsorption on bentonite clay, few studies have been carried out. Bekçi et al. (2006) and Qtaitat (2004) found that montmorillonite exhibits a high adsorption capacity for TMP, which is mainly controlled by electrostatic attractions. On the other hand, Li et al. (2011) and Lv et al. (2012) investigated the adsorption of

CPA on montmorillonite and obtained a good adsorption capacity influenced by electrostatic attractions and cation exchange. So far, existing studies in this field have been general, and the influence of chemical, textural, and swelling properties of bentonite on the adsorption capacity of these pharmaceuticals from water has not been investigated in detail. Furthermore, the reversibility of adsorption and the possibility of regeneration and reuse of bentonite have not been thoroughly addressed.

The main objective of Chapter 5 is to investigate the effect of the chemical, textural, and swelling properties of bentonite on the adsorption of TMP and CPA. To achieve this, samples of bentonite equilibrated with TMP and CPA in different uptakes adsorbed were prepared and characterized by N<sub>2</sub> physisorption, scanning electron microscopy, Zeta potential, and XRD techniques, and the uptake of cations exchanged during the adsorption was performed. In addition, adsorption isotherms were obtained to show the influence of operating variables (pH, temperature, and ionic strength of the solution) on the sorption process. The adsorption reversibility was also studied to determine the feasibility of regeneration and reuse of this clay.

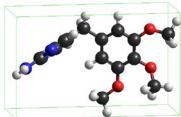
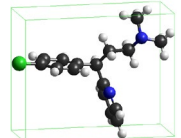
## **5.2 Experimental methodology**

### **5.2.1 Pharmaceutical compounds**

Cationic pharmaceuticals such as trimethoprim (TMP) (CAS: 738-70-5) and chlorphenamine (CPA) (CAS: 113-92-8) were supplied by Merck. Table 5.1 contains the physicochemical properties of these compounds.

In aqueous solutions, TMP and CPA release protons and present distinct chemical species based on the solution pH. Figure 5.1 illustrates the chemical species distribution diagrams of TMP and CPA at a total concentration of 0.5 mmol/L. TMP exists in two chemical species: the cationic form (TMP<sup>+</sup>) at pH levels below 7.16, and the neutral species (TMP<sup>0</sup>) above 7.16. In contrast, CPA exhibits three chemical species: at pH values below 4.0, the di-cationic species (CPA<sup>2+</sup>) predominates; between pH 4.0 and 9.2 exists the cationic species (CPA<sup>+</sup>), and above 9.2, the neutral species (CPA<sup>0</sup>) prevails.

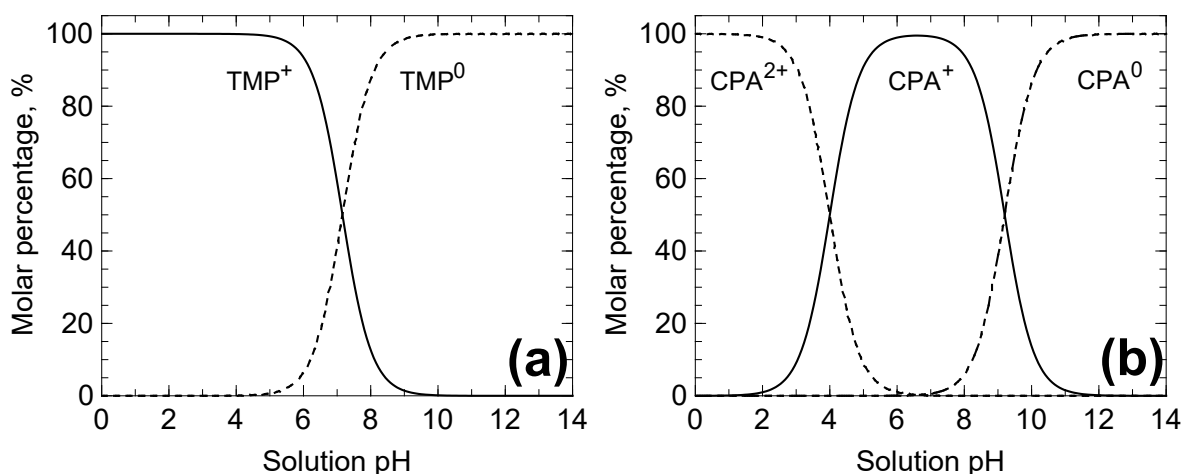
**Table 5.1.** Physicochemical properties of TMP and CPA.

| Solutes                                  | Family         | Molecular structure <sup>a</sup>                                                  | Molecular size <sup>a</sup><br>(nm) | Log D <sup>b</sup> | pK <sub>a</sub> <sup>c</sup> |
|------------------------------------------|----------------|-----------------------------------------------------------------------------------|-------------------------------------|--------------------|------------------------------|
| Trimethoprim<br>(TMP)<br>M.W. = 290.32   | Antibiotics    |  | X = 1.19<br>Y = 0.74<br>Z = 0.52    | 0.92               | 7.16                         |
| Chlorphenamine<br>(CPA)<br>M.W. = 274.79 | Antihistamines |  | X = 1.11<br>Y = 0.91<br>Z = 0.49    | 1.15               | 4.00, 9.20                   |

<sup>a</sup> Determined by Density Functional Theory (DFT) using 6-31G B3LYP method.

<sup>b</sup> Distribution coefficients at pH = 7.

<sup>c</sup> Dissociation constants.



**Figure 5.1.** Chemical species distribution diagrams of TMP (a) and CPA (b) at a total concentration of 0.5 mmol/L.

### 5.2.2 Method for quantifying TMP and CPA concentrations

The concentrations of TMP and CPA in aqueous solutions were determined using a Shimadzu 2600 UV-Vis spectrophotometer. Calibration curves were generated using standard solutions prepared at concentrations ranging from 0.6 to 60 mg/L for TMP and from 0.5 to 50 mg/L for CPA. The analytical method involves the measurement of absorbances at wavelengths of 271 nm for TMP and 261 nm for CPA.

### 5.2.3 Materials and characterization

Bentonite (Bent) used in this study is a calcium clay composed mainly of the montmorillonite phase. The extraction and conditioning procedure of Bent, as well as its chemical composition, have been described in detail in Chapter 4.

Bent samples were saturated with TMP and CPA at different uptakes adsorbed. The nomenclature and specifications of the prepared samples are detailed in Table 5.2, expressed in units of centimoles of positive charge per kilogram of clay (cmol(+)/kg), and the equivalence in milligrams per gram of clay (mg/g).

**Table 5.2.** Prepared samples of Bent saturated with TMP and CPA at different uptakes of the pharmaceuticals adsorbed.

| Bent saturated with TMP |                 |        | Bent saturated with CPA |                 |        |
|-------------------------|-----------------|--------|-------------------------|-----------------|--------|
| Nomenclature            | Uptake adsorbed |        | Nomenclature            | Uptake adsorbed |        |
|                         | (cmol(+)/kg)    | (mg/g) |                         | (cmol(+)/kg)    | (mg/g) |
| B-TMP-3                 | 3               | 8.7    | B-CPA-6                 | 6               | 16.5   |
| B-TMP-20                | 20              | 58.1   | B-CPA-20                | 20              | 54.9   |
| B-TMP-30                | 30              | 87.1   | B-CPA-35                | 35              | 96.2   |
| B-TMP-40                | 40              | 116.1  | B-CPA-45                | 45              | 123.6  |
| B-TMP-50                | 50              | 145.2  | B-CPA-52                | 52              | 142.9  |

The textural properties of the samples were estimated using a Micromeritics N<sub>2</sub> physisorption analyzer, model ASAP 2020. The analysis involved obtaining the N<sub>2</sub> adsorption-desorption isotherms at -196.15 °C. The morphology of the samples was observed in a JEOL scanning electron microscope, model JSM-6610LV. In addition, the swelling capability of the samples was analyzed by XRD in a Rigaku X-ray diffractometer, model Ultima IV. The X-ray diffraction patterns were acquired under the following operating conditions: Cu-K $\alpha$  ( $\lambda$  = 0.15406 nm), 44 mA and 40 kV, and the measurements were taken from 3 to 50 ° (2 $\theta$ ) at a scan speed of 1.8 °/min.

The surface charge distribution of Bent was determined using the procedure described in Chapter 4. The Zeta potential of the samples of Bent saturated with TMP and CPA at different uptakes adsorbed was obtained at a constant pH value.

Dispersions of Bent in solutions with TMP or CPA concentrations ranging from 5 to 200 mg/L were prepared, maintaining an ionic strength of 0.01 N at pH 5 for TMP and 7 for CPA. These pH values were chosen because they correspond to the pH values where TMP and CPA prevails as cations (Figure 5.1). Subsequently, 0.01 g of Bent was mixed with 40 mL of each TMP or CPA solution for 8 days, keeping pH constant. Finally, the Zeta potential of these suspensions was measured according to the procedure described in Chapter 4.

The uptake of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  cations and  $\text{H}^+$  ion exchanged during the adsorption of TMP, or CPA on Bent was determined as a function of the uptake of TMP and CPA adsorbed. The two-step method described in Chapter 4 was employed for this analysis.

#### **5.2.4 Procedure for obtaining adsorption and desorption equilibrium data**

Experimental adsorption and desorption equilibrium data were obtained using batch adsorbers (Figure 4.2). The procedure follows a methodology similar to that described in Chapter 4.

#### **5.2.5 Method for performing reuse cycles and regeneration of Bent**

The reusability of Bent for the adsorption of TMP and CPA was assessed through reuse and regeneration cycles. The experimental procedures were performed according to the outlined steps. Initially, the adsorption equilibrium of TMP or CPA was achieved by the detailed procedure described in Chapter 4. Subsequently, the uptake of TMP or CPA adsorbed on Bent was calculated using the mass balance of Equation (4.2), designated as the uptake adsorbed in cycle 1 ( $q_{C1}$ ). After reaching adsorption equilibrium, the Bent particles were separated from the solution and subjected to multiple washes with isopropanol (IPA) to remove excess TMP or CPA. The cleaned Bent was then immersed in a 40 mL of basic (pH = 11) free-drug solution to initiate the regeneration cycle. This suspension was left in contact for 8 days, with the pH of the solution being adjusted daily. After this time, the concentration of TMP or CPA in the solution was measured, and the uptake of TMP or CPA remaining adsorbed was



estimated using Equation (4.3). This uptake was referred to as the uptake adsorbed for regeneration cycle 1 ( $q_{R1}$ ). Subsequently, the clay was removed from the solution, washed multiple times with IPA, and dried at 30 °C for 72 h. The adsorption and desorption process were repeated under the same conditions as described earlier to perform the subsequent reuse and regeneration cycle. The reuse of Bent for the sorption of TMP or CPA was evaluated by completing a total of 5 cycles of reuse and regeneration. The reuse and regeneration percentages were calculated using the following equations:

$$\%Reu = \frac{q_{Ci}}{q_{C1}} \times 100 \% \quad (5.1)$$

$$\%Reg = \frac{q_{Ci}}{q_{C1}} - \frac{q_{Ci}}{q_{Ri}} \times 100 \% \quad (5.2)$$

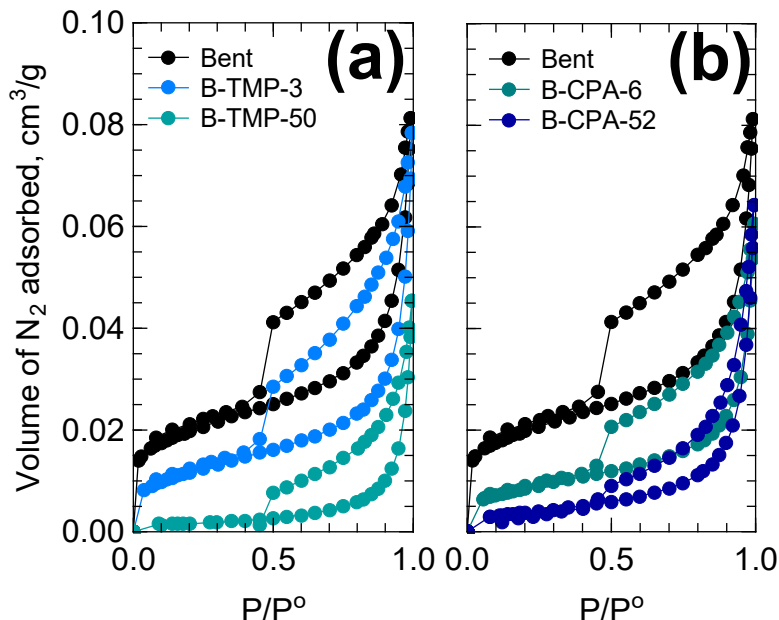
where  $q_{Ci}$  is the uptake of TMP or CPA adsorbed in reuse cycle  $i$ , mg/g;  $q_{C1}$  is the uptake of TMP or CPA adsorbed in the first reuse cycle, mg/g;  $q_{Ri}$  is the uptake of TMP or CPA that remained adsorbed in regeneration cycle  $i$ , mg/g; %Reu and %Reg are the reuse and regeneration percentages, respectively.

## **5.3 Results and discussion**

### **5.3.1 Influence of textural and morphological properties of bentonite for the adsorption of TMP and CPA**

Figure 5.2 displays N<sub>2</sub> adsorption-desorption isotherms onto Bent and Bent equilibrated with different uptakes of TMP or CPA adsorbed. According to the IUPAC classification (Rouquerol et al., 1998), these isotherms fall into the IIb category, which is characterized by an H3 hysteresis loop and the absence of a plateau at high  $P/P^0$  values, indicating mesoporous materials composed of aggregated laminar particles (Gregg and Sing, 1982). The mesoporosity observed in Bent is ascribed to the random arrangement of the laminar blocks (Rouquerol et al., 1998). As for Bent equilibrated with TMP and CPA adsorbed, the N<sub>2</sub> adsorption-desorption isotherms exhibit remarkable similarities. They show a reduction in the volume of N<sub>2</sub> adsorbed as the uptake of TMP or CPA adsorbed increases, accompanied by a narrower hysteresis

loop. This finding reveals that TMP and CPA molecules hinder the accessibility of mesopores since the adsorption mainly occurs on mesopores.



**Figure 5.2.** Adsorption-desorption isotherms of N<sub>2</sub> on Bent, B-TMP (a) and B-CPA (b) samples at -196.15 °C.

Table 5.3 lists the textural properties of Bent and the prepared samples of Bent with different uptakes of TMP and CPA adsorbed. The results revealed a significant decrease in  $S_{\text{BET}}$  alongside an increase in  $D_p$  as the uptake of TMP and CPA adsorbed was raised in comparison with Bent. Moreover, the values of  $S_{\text{meso}}$  diminished notably with the increasing uptakes of TMP and CPA adsorbed. In the samples labeled as B-TMP, a reduction in both  $V_p$  and  $V_{\text{meso}}$  was observed as the uptake of TMP adsorbed raised. Conversely, in the B-CPA samples, the values of  $V_p$  and  $V_{\text{meso}}$  remained relatively constant as the uptake of CPA augmented. These findings indicate that these pharmaceuticals are primarily adsorbed onto the sites located within the mesopores of Bent but in different molecular orientations. Furthermore, they underscore the significance of the textural properties of Bent in the adsorption of the TMP and CPA pharmaceuticals.

**Table 5.3.** Textural properties of Bent and the prepared samples of Bent saturated with different uptakes of TMP and CPA adsorbed.

| Samples  | $S_{BET}^a$<br>(m <sup>2</sup> /g) | $V_p^b$<br>(cm <sup>3</sup> /g) | $D_p$<br>(nm) | $S_{meso}^c$<br>(m <sup>2</sup> /g) | $V_{meso}^d$<br>(cm <sup>3</sup> /g) |
|----------|------------------------------------|---------------------------------|---------------|-------------------------------------|--------------------------------------|
| Bent     | 45                                 | 0.087                           | 7.8           | 32                                  | 0.075                                |
| B-TMP-3  | 27                                 | 0.078                           | 11.7          | 25                                  | 0.073                                |
| B-TMP-20 | 9                                  | 0.050                           | 22.2          | 9                                   | 0.039                                |
| B-TMP-50 | 4                                  | 0.045                           | 49.4          | 4                                   | 0.046                                |
| B-CPA-6  | 19                                 | 0.061                           | 12.5          | 18                                  | 0.054                                |
| B-CPA-20 | 13                                 | 0.067                           | 20.3          | 13                                  | 0.056                                |
| B-CPA-52 | 9                                  | 0.064                           | 29.2          | 9                                   | 0.059                                |

<sup>a</sup> Specific surface area determined by the BET method.

<sup>b</sup> Total pore volume evaluated by the Gurvich rule at  $P/P^0 = 0.99$ .

<sup>c</sup> Mesoporous area calculated by the t-plot method.

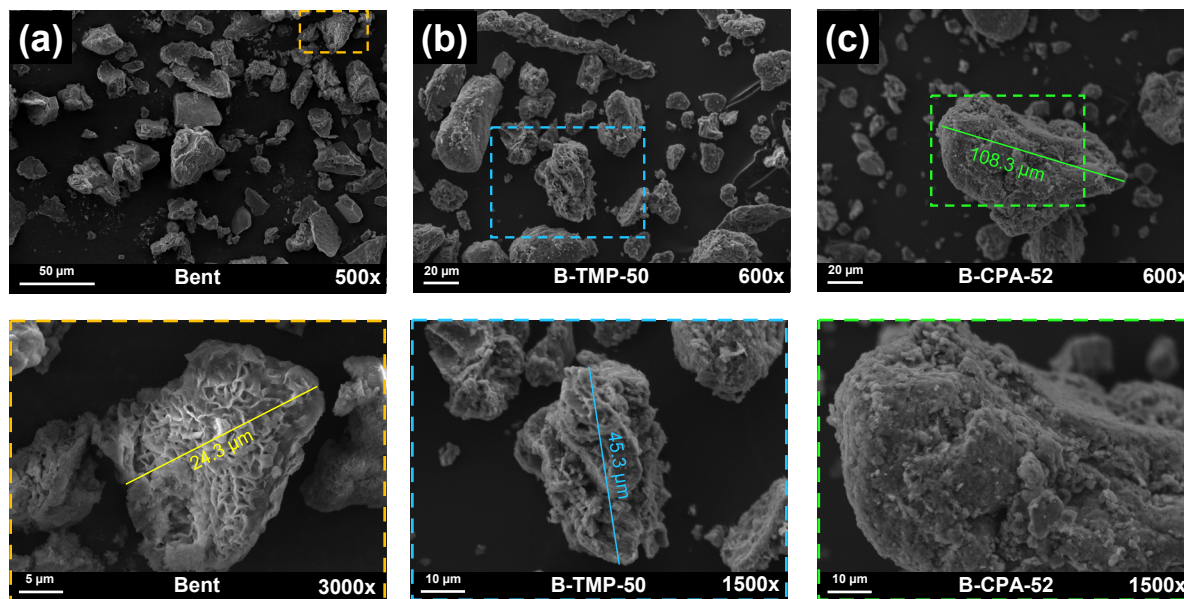
<sup>d</sup> Mesoporous volume obtained by the BJH method.

The SEM image of Bent reveals plate-like aggregates with sizes smaller than 30  $\mu\text{m}$ , as illustrated in Figure 5.3. From the highlighted yellow region and at higher magnification, Bent exhibits an open texture because of randomly arranged thin laminar particles. In addition, Figures 5.3 (b) and 5.3 (c) depict SEM images of the B-TMP-50 and B-CPA-52 samples, along with magnified views of the areas highlighted in blue and green, respectively, providing clear evidence of remarkable alterations in the morphology of Bent after the adsorption of TMP and CPA. The open texture of Bent was hindered or blocked by pharmaceuticals, which promoted the formation of clusters on the external mesopores and produced a marked increase in particle size, reaching 45.3 and 108.3  $\mu\text{m}$  for the B-TMP-50 and B-CPA-52 samples, correspondingly.

### 5.3.2 Impact of the surface charge of bentonite for the adsorption of TMP and CPA

The chemical composition of Bent via isomorphic substitution of cations plays an essential role in the residual charge of its structure, which affects the surface charge of particles in aqueous solutions, impacting adsorption processes. Figure 5.4 (a)

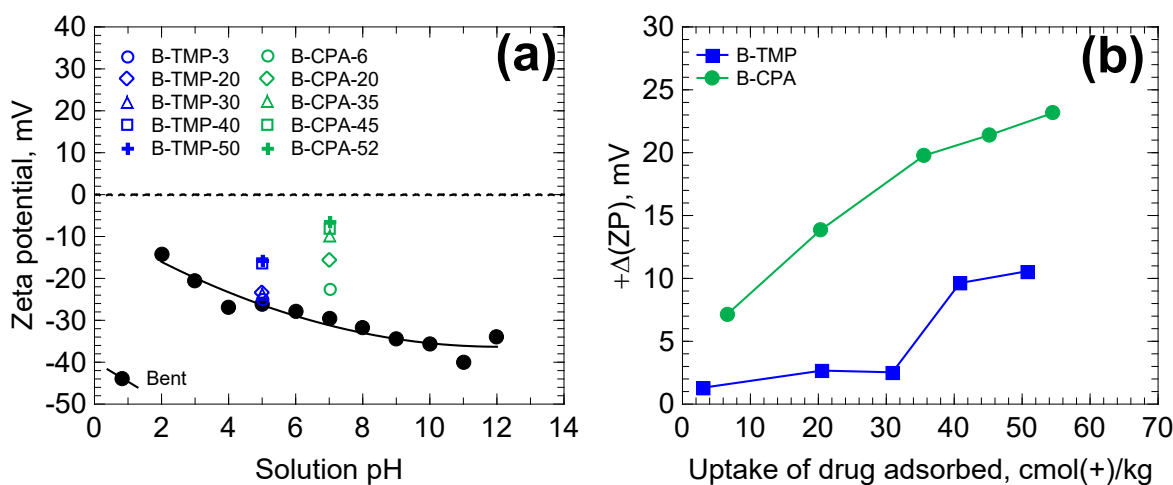
illustrates the surface charge distribution of Bent (represented by black markers), revealing that Bent exhibits a negative charge across the entire pH range of the solution studied. This negative charge becomes more pronounced as the pH of the solution increases, as evidenced by the Zeta potential values varying from -14 (pH = 2) to -36 mV (pH = 12). Even if the value of the isoelectric point ( $\text{pH}_{\text{IEP}}$ ) could not be precisely determined, the figure suggests that it is below 2. The negative charge observed for the Bent surface is attributed to isomorphous substitutions occurring in its tetrahedral and octahedral layers, which results in an excess of negative charge in its structure. During the substitution process,  $\text{Si}^{4+}$  in the tetrahedral layers is replaced by other cations with lower oxidation states, such as  $\text{Al}^{3+}$ , while  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$  can substitute high oxidation state cations in the octahedral layers,  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  (Emmerich, 2013).



**Figure 5.3.** SEM images of Bent (a), B-TMP-50 (b) and B-CPA-52 (c) at different magnifications.

In addition, the uptake of TMP and CPA adsorbed on Bent affects the surface charge, as illustrated Figure 5.4 (a). The experiments were conducted at pH 5 for TMP and 7 for CPA since the pharmaceutical species prevails as positively charged at these pH values (Figure 5.1). The figure shows that the uptake adsorbed modifies the surface charge, makes it less negative as the uptake adsorbed of TMP and CPA increases.

Here, a significant variation in the surface charge of Bent was observed with increasing the uptake of CPA adsorbed; for example, the Zeta potential value changed from -30 to -6 mV for Bent and B-CPA-52, respectively. As for TMP adsorption, the surface charge of Bent shifted from -26 to -15 mV for Bent and B-TMP-50, correspondingly. To examine the variation of the surface charge of Bent as a function of the uptake adsorbed,  $Q_A$ , the Zeta potential gradient,  $\Delta(ZP)$  (mV), was calculated. The values of  $Q_A$ , in cmol(+)/kg units, were determined using the mass balance from Equation (4.4), and  $\Delta(ZP)$  was estimated using the Equation (4.8). The  $\Delta(ZP)$  increases with the uptake of TMP or CPA adsorbed on Bent, as depicted Figure 5.4 (b). The positive value of  $\Delta(ZP)$  indicates that the surface charge of Bent becomes less negative due to the adsorption of  $TMP^+$  and  $CPA^+$  onto the cationic sites of the clay, effectively neutralizing its surface charge. These results highlight that electrostatic attractions significantly contribute to the adsorption of TMP and CPA on Bent.

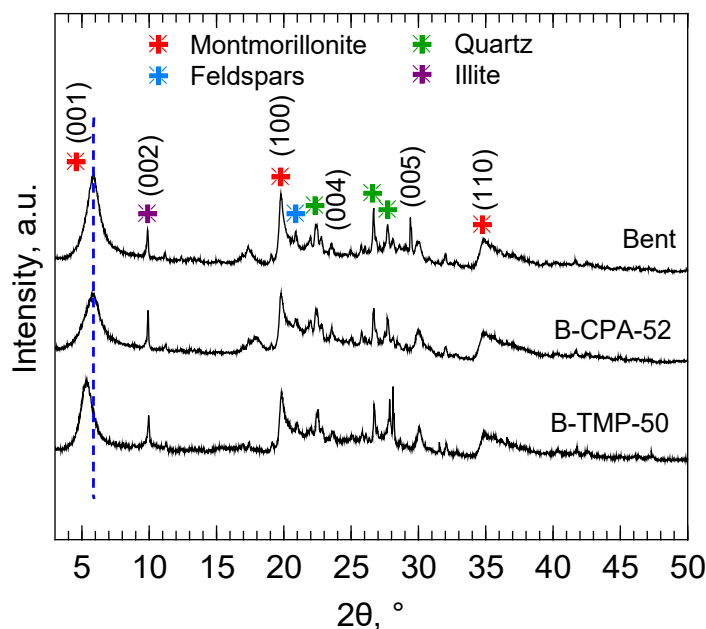


**Figure 5.4.** Surface charge distribution of Bent and B-TMP and B-CPA with different uptakes of pharmaceuticals adsorbed (a). Variation of the Zeta potential as a function of the uptake of TMP and CPA adsorbed on Bent (b).

### 5.3.3 Importance of swelling capability of bentonite for the adsorption of TMP and CPA

The XRD patterns of Bent, B-TMP-50 and B-CPA-52 are shown in Figure 5.5. Comparison of these XRD patterns with the JCPDS 13-0135 standard confirmed that

the reflections correspond to the montmorillonite phase at 5.89, 19.72, and 34.74 ° (2 $\theta$ ), associated with the (001), (100), and (110) crystallographic planes, respectively (Orolínovaá et al., 2010; Zhang et al., 2017). Besides, the presence of feldspars and quartz was detected within the 20 to 29 ° (2 $\theta$ ) interval, along with illite at the 9.8 ° (2 $\theta$ ) position (Elgamouz et al., 2019; Marsh et al., 2018).

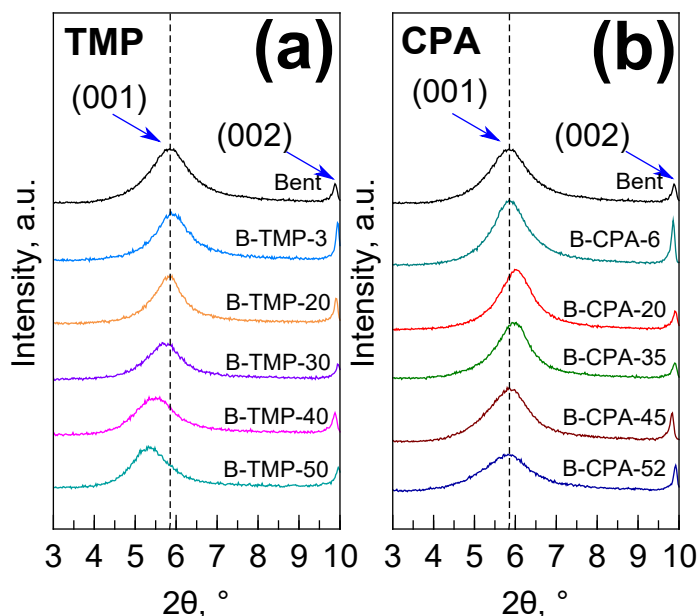


**Figure 5.5.** XRD patterns of Bent, B-TMP-50 and B-CPA-52.

The basal spacing of the (001) plane in Bent, denoted as  $d_{001}$ , measured to be 1.50 nm, is attributed to the hydration water molecules of the interlayer cations located within the interlayer space of Bent. The figure also illustrates that the reflection of the (001) plane in B-TMP-50 notably shifted towards lower angles, whereas its position in B-CPA-52 showed no apparent displacement.

Figure 5.6 displays XRD patterns of Bent and Bent samples with varying uptakes of TMP and CPA adsorbed in the (2 $\theta$ ) range from 3 to 10°. As shown in Figure 5.6 (a), the (001) reflection shifts progressively to lower 2 $\theta$  angles as a function of the uptake of TMP adsorbed, which is noticeable for B-TMP-30 and the other samples with higher uptakes of TMP. In Figure 5.6 (b), the (001) reflection shifted slightly toward higher angles as the uptake of CPA adsorbed augmented up to the B-CPA-35 sample;

however, by raising the uptake of CPA adsorbed, the position of this reflection returns to that determined for the B-CPA-6 and unsaturated Bent.



**Figure 5.6.** XRD patterns of Bent and B-TMP and B-CPA samples with different uptakes of TMP (a) and CPA (b) adsorbed in the 3 – 10° ( $2\theta$ ) interval where the (001) reflection of Bent appears.

The  $d_{001}$  values were determined using Bragg's law, which combines the interlayer distance ( $d$ ) and the thickness of the trilaminar block ( $t$ ). A study estimated the thickness of the trilaminar block of Bent to be 0.96 nm (Moore and Hower, 1986). Therefore, the interlayer distance was calculated by subtracting the thickness of the trilaminar block from  $d_{001}$ . The  $d_{001}$  and  $d$  values for Bent and Bent saturated with different uptakes of TMP and CPA adsorbed are given in Table 5.4. As for the B-TMP samples, the  $d$  values remained constant until the B-TMP-20 sample. Nevertheless, as the uptake of TMP adsorbed raised, the values of  $d$  increased to 0.70 nm in B-TMP-50, indicating an expansion of the interlayer spacing of Bent due to TMP adsorption. In the B-CPA samples, the  $d$  values decreased slightly as the uptake of CPA adsorbed augmented in B-CPA-20 and B-CPA-35, suggesting a contraction of the interlayer spacing of Bent due to CPA adsorption. However, by further increasing the uptake of

CPA adsorbed, the  $d$  values of the B-CPA-45 and B-CPA-52 samples raised and returned to the initial interlayer spacing of unsaturated Bent.

**Table 5.4.** Values of basal distances ( $d_{001}$ ) and interlayer spacings ( $d$ ) corresponding to the Bent and Bent saturated with different uptakes of TMP and CPA adsorbed.

| Sample   | $d_{001}$<br>(nm) | $d$<br>(nm) | Sample   | $d_{001}$<br>(nm) | $d$<br>(nm) |
|----------|-------------------|-------------|----------|-------------------|-------------|
| Bent     | 1.50              | 0.54        |          |                   |             |
| B-TMP-3  | 1.50              | 0.54        | B-CPA-6  | 1.50              | 0.54        |
| B-TMP-20 | 1.50              | 0.54        | B-CPA-20 | 1.47              | 0.51        |
| B-TMP-30 | 1.56              | 0.60        | B-CPA-35 | 1.46              | 0.50        |
| B-TMP-40 | 1.61              | 0.65        | B-CPA-45 | 1.49              | 0.53        |
| B-TMP-50 | 1.66              | 0.70        | B-CPA-52 | 1.50              | 0.54        |

Table 5.1 contains the molecular sizes of TMP and CPA. Here, the Z dimension of the CPA molecule is 0.49 nm, which is very similar to the interlayer spacing value of the B-CPA-35 sample (0.50 nm), indicating that CPA molecules intercalate into the interlayer space of Bent in an orientation parallel to its transverse XY area, and conducting to the contraction of the layers of Bent, since the Z dimension of CPA is smaller than that of the interlayer spacing of Bent (0.54 nm). Furthermore, the increase in the interlayer spacing in the B-CPA-45 and B-CPA-52 samples may be related to the higher number of CPA molecules intercalated into the interlayer surface of Bent.

Regarding the adsorption of TMP onto Bent, the Y and Z dimensions of TMP are 0.74 and 0.52 nm, respectively (Table 5.1), and the interlayer spacings remain constant (0.54 nm) in the B-TMP-3 and B-TMP-20 samples because TMP intercalates parallel to its transverse XY area, as its Z dimension (0.52 nm) closely matches the interlayer spacing of Bent (0.54 nm). In the case of the B-TMP-50, there was an expansion in the interlayer spacing of Bent (0.70 nm) due to TMP molecules are adsorbed in the interlayer space in an orientation parallel to their XZ area, where the Y dimension of TMP (0.74 nm) aligns with the interlayer spacing of B-TMP-50 (0.70 nm). Similar results



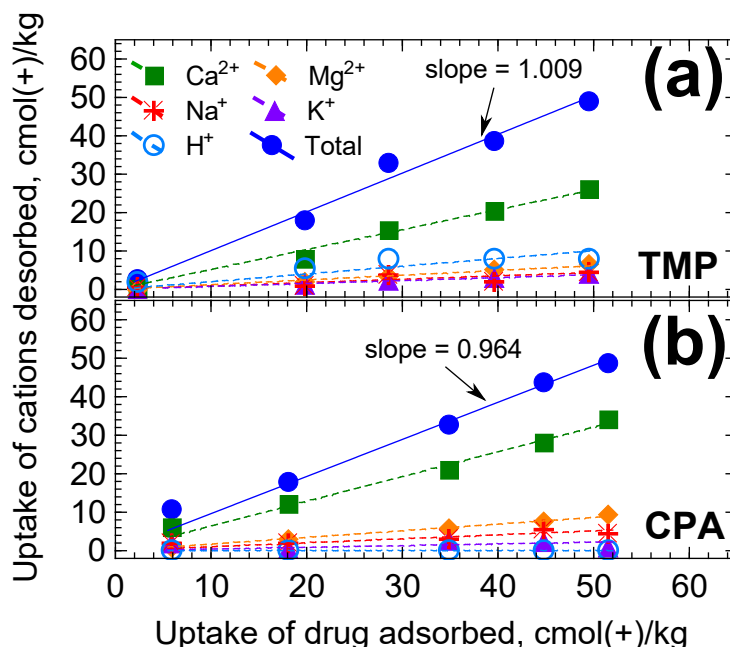
were previously reported in a study about the adsorption mechanisms of tetracycline onto Ca-bentonite (Ortiz-Ramos et al., 2022).

These findings highlight the importance of the swelling ability of Bent in the adsorption of TMP and CPA, which is also strongly influenced by their molecular size and uptake adsorbed.

#### **5.3.4 Effect of the cation exchange capacity of bentonite for the adsorption of TMP and CPA**

The cation exchange capacity (CEC) of Bent was estimated according to the method proposed by Ming and Dixon (1987), obtaining a value of 75 cmol(+)/kg. To analyze the uptake of cations exchanged during the adsorption of TMP and CPA on Bent, the concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ , and  $\text{H}^{+}$  cations in the solution was determined before and after the adsorption of TMP or CPA. Subsequently, the uptake of cations desorbed or exchanged was calculated as a function of the uptake of TMP or CPA adsorbed, using Equations (4.4-4.6). The total uptake of cations desorbed increased linearly with the uptake of TMP and CPA adsorbed and remained below the CEC value of Bent in all cases, as illustrated in Figure 5.7. The linear fit of the experimental data reveals a slope very close to 1, with a value of 1.009 for TMP and 0.964 for CPA, which indicates that for every 1 cmol(+)/kg of TMP or CPA adsorbed, approximately 1 cmol(+)/kg of cations are desorbed. For instance, an uptake of 44.8 cmol(+)/kg of CPA adsorbed resulted in a total cations desorption of 43.7 cmol(+)/kg (Figure 5.7 (b)). Furthermore,  $\text{Ca}^{2+}$  was the predominant cation exchanged, and the uptake of cations desorbed diminished in the following order:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{+} > \text{K}^{+} >> \text{H}^{+}$ . The desorption of  $\text{H}^{+}$  ions was relatively low because the pH of the solution remained very close to 7 throughout the experiment. Figure 5.7 (a) exhibited a similar behavior for TMP adsorption.

These results underscore the influence of interlayer cations of Bent on TMP and CPA adsorption, establishing the essential role of CEC and electrostatic attraction in the adsorption mechanism of TMP and CPA. In addition, these findings correlate with the outcomes obtained from XRD analysis.



**Figure 5.7.** Uptake of cations desorbed or exchanged as a function of the uptake of TMP (a) or CPA (b) adsorbed on Bent at T = 25 °C. The lines represent a linear fit of the experimental data.

### 5.3.5 Adsorption isotherms

The adsorption isotherms of TMP and CPA on Bent were constructed to analyze the effect of pH, ionic strength and solution temperature on the adsorption capacity. Furthermore, the reversibility of TMP and CPA adsorption onto Bent studies were performed. The experimental data of adsorption equilibrium were interpreted using the Freundlich, Langmuir and Radke-Prausnitz adsorption isotherm models, described by the Equations (4.9-4.11).

Table 5.5 lists the parameters obtained for the TMP and CPA adsorption isotherms on Bent under different experimental conditions of pH, ionic strength, and solution temperature. It also includes the average percentage deviation obtained for each adsorption isotherm model, calculated using Equation (4.12).

The results presented in the tables indicate that the Freundlich adsorption isotherm model did not adequately fit the experimental data, as it yielded very high average percentage deviation in most cases. Conversely, the Langmuir and Radke-

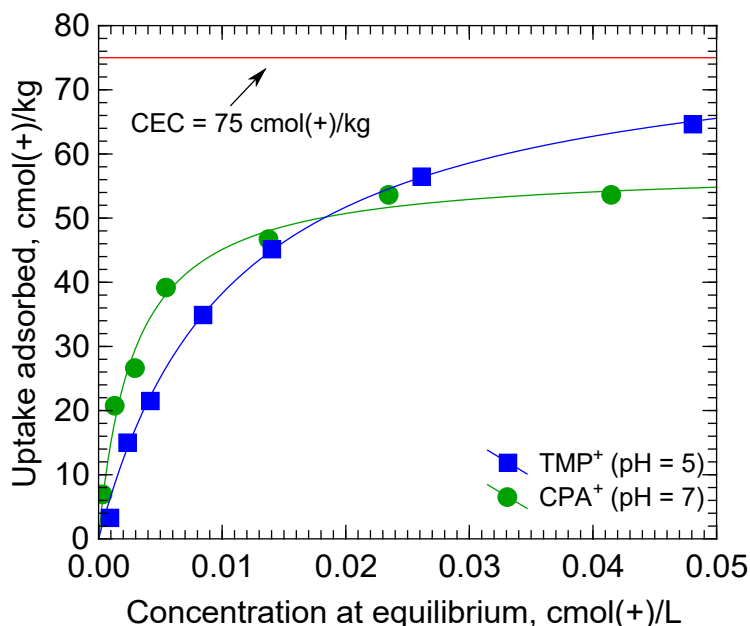
Prausnitz models showed a good fit of the experimental data, achieving average percentage deviation below 16.6 %. Based on these results, the Langmuir model was selected to interpret the adsorption isotherm data since most of the  $\beta$  values in the Radke-Prausnitz model are close to 1, indicating that the Radke-Prausnitz isotherm is practically equivalent to the Langmuir isotherm.

**Table 5.5.** Adsorption isotherm parameters and average percentage deviation for the adsorption of TMP and CPA on Bent.

| Solutes | pH | I<br>(N) | T<br>(°C) | Freundlich                                     |      |      | Langmuir                 |             |      | Radke-Prausnitz |                                         |      |      |
|---------|----|----------|-----------|------------------------------------------------|------|------|--------------------------|-------------|------|-----------------|-----------------------------------------|------|------|
|         |    |          |           | K<br>(mg <sup>1-1/n</sup> L <sup>1/n</sup> /g) | n    | %D   | q <sub>m</sub><br>(mg/g) | K<br>(L/mg) | %D   | a<br>(L/g)      | b<br>(L <sup>β</sup> /mg <sup>β</sup> ) | β    | %D   |
| TMP     | 3  | 0.01     | 25        | 23.08                                          | 2.31 | 43.7 | 220.44                   | 0.036       | 12.5 | 7.85            | 0.036                                   | 1.00 | 12.5 |
|         | 5  | 0.01     | 25        | 21.70                                          | 2.21 | 40.8 | 231.62                   | 0.032       | 11.8 | 7.35            | 0.032                                   | 1.00 | 11.8 |
|         | 7  | 0.01     | 25        | 2.92                                           | 1.26 | 5.8  | 426.29                   | 0.004       | 9.0  | 1.55            | 0.004                                   | 1.00 | 9.0  |
|         | 9  | 0.01     | 25        | 0.24                                           | 1.27 | 22.1 | 31.01                    | 0.004       | 12.6 | 0.13            | 0.004                                   | 1.00 | 12.6 |
|         | 11 | 0.01     | 25        | 0.07                                           | 1.14 | 17.0 | 23.79                    | 0.002       | 13.7 | 0.05            | 0.002                                   | 1.00 | 13.7 |
|         | 5  | 0.1      | 25        | 6.19                                           | 1.45 | 29.8 | 314.46                   | 0.009       | 16.6 | 2.81            | 0.009                                   | 1.00 | 16.6 |
|         | 5  | 0.5      | 25        | 1.31                                           | 1.04 | 8.2  | 980.76                   | 0.001       | 8.2  | 1.22            | 0.001                                   | 1.00 | 8.2  |
|         | 5  | 0.01     | 15        | 17.88                                          | 1.99 | 32.5 | 243.86                   | 0.027       | 9.5  | 6.43            | 0.026                                   | 1.00 | 9.5  |
|         | 5  | 0.01     | 35        | 18.07                                          | 1.91 | 19.7 | 271.53                   | 0.025       | 6.7  | 6.69            | 0.025                                   | 1.00 | 6.7  |
|         | 5  | 0.01     | 25        | 18.07                                          | 1.91 | 19.7 | 271.53                   | 0.025       | 6.7  | 6.69            | 0.025                                   | 1.00 | 6.7  |
| CPA     | 7  | 0.01     | 25        | 40.68                                          | 3.40 | 23.4 | 159.18                   | 0.128       | 5.1  | 21.50           | 0.148                                   | 0.98 | 4.7  |
|         | 8  | 0.01     | 25        | 39.12                                          | 3.23 | 23.8 | 163.79                   | 0.116       | 5.5  | 20.53           | 0.144                                   | 0.97 | 5.1  |
|         | 9  | 0.01     | 25        | 31.65                                          | 2.75 | 25.9 | 180.71                   | 0.067       | 6.0  | 12.56           | 0.069                                   | 1.00 | 6.0  |
|         | 10 | 0.01     | 25        | 13.63                                          | 2.58 | 16.8 | 91.53                    | 0.051       | 7.0  | 4.72            | 0.051                                   | 1.00 | 7.0  |
|         | 11 | 0.01     | 25        | 3.67                                           | 2.11 | 9.1  | 47.95                    | 0.021       | 9.3  | 1.85            | 0.167                                   | 0.72 | 8.1  |
|         | 7  | 0.1      | 25        | 22.17                                          | 2.79 | 27.3 | 138.04                   | 0.051       | 11.6 | 7.09            | 0.051                                   | 1.00 | 11.6 |
|         | 7  | 0.5      | 25        | 4.52                                           | 1.54 | 15.2 | 179.40                   | 0.010       | 8.2  | 1.84            | 0.010                                   | 1.00 | 8.2  |
|         | 7  | 0.01     | 15        | 31.37                                          | 3.15 | 30.6 | 150.05                   | 0.080       | 13.0 | 12.02           | 0.080                                   | 1.00 | 13.0 |
|         | 7  | 0.01     | 35        | 27.25                                          | 2.72 | 24.7 | 164.21                   | 0.064       | 9.6  | 10.49           | 0.064                                   | 1.00 | 9.6  |
|         | 7  | 0.01     | 25        | 27.25                                          | 2.72 | 24.7 | 164.21                   | 0.064       | 9.6  | 10.49           | 0.064                                   | 1.00 | 9.6  |

Figure 5.8 illustrates the adsorption isotherms of TMP and CPA on Bent at I = 0.01 N and T = 25 °C. To compare the adsorption capacity of Bent toward both pharmaceuticals, the uptake adsorbed was expressed in units of cmol(+)/kg, and the cation exchange capacity of Bent was graphed with a continuous red line. Experimental data were obtained at the pH corresponding to the predominant cationic species of both pharmaceuticals; thus, the adsorption of TMP was evaluated at pH 5, while that of CPA was performed at pH 7 (see Figure 5.1). The findings indicated that Bent exhibits

significant capacities for adsorbing TMP and CPA. The maximum adsorption capacities recorded were 64.2 (186.5 mg/g) and 58.1 cmol(+)/kg (159.8 mg/g) for TMP and CPA, respectively, which were lower than the CEC of Bent, 75 cmol(+)/kg. These values are comparable to or even surpass those reported in the literature for various adsorbent materials (Table 5.6). Although Bent demonstrated a greater capacity to adsorb CPA than TMP at equilibrium concentrations below 0.018 cmol(+)/L, it showed a superior adsorption capacity toward TMP than for CPA at higher equilibrium concentrations.



**Figure 5.8.** Adsorption isotherms of TMP and CPA on Bent at  $I = 0.01$  N and  $T = 25$  °C. The red line represents the CEC of Bent, 75 cmol(+)/kg, while the blue and green lines represent the Langmuir adsorption isotherms.

The maximum uptake adsorbed of TMP and CPA onto Bent is attributed to the structural arrangement, the interlayer cations-types, cation exchange capacity, and swelling ability of the clay. The adsorption of the TMP and CPA cations occurs through electrostatic attractions due to the negative surface charge of Bent ( $pH_{IEP} < 2$ ), as observed in Figure 5.4. In addition to electrostatic attractions, cation exchange reactions between TMP and CPA and the interlayer cations of Bent also contribute significantly to the adsorption mechanism as illustrated in Figure 5.7; these reactions

lead to the adsorption on the interlayer spacing of Bent, as evidenced in Figure 5.6, but also on its mesopore surface, as demonstrated in Figure 5.2.

**Table 5.6.** Capacities of different materials for adsorbing TMP and CPA.

| Adsorbents                                                    | Solutes    | Maximum adsorption capacity (mg/g) | Experimental conditions  | Reference                       |
|---------------------------------------------------------------|------------|------------------------------------|--------------------------|---------------------------------|
| Graphene oxide                                                | TMP        | 218.0                              | pH = 10, T = 25 °C       | Carrales-Alvarado et al. (2020) |
| <b>Bentonite clay</b>                                         | <b>TMP</b> | <b>186.6</b>                       | <b>pH = 5, T = 25 °C</b> | <b>This work</b>                |
| Activated carbon                                              | TMP        | 125.9                              | pH = 6, T = 25 °C        | Berges et al. (2021)            |
| MgO-Al <sub>2</sub> O <sub>3</sub> modified rice husk biochar | TMP        | 54.2                               | pH = 6, T = 10 °C        | Chaubey et al. (2023)           |
| Biocomposite based on peanut husk                             | TMP        | 20.3                               | pH = 5, T = 19.8 °C      | Aryee et al. (2021)             |
| Residual carbon                                               | TMP        | 5.0                                | pH = 8, T = 25 °C        | Xue et al. (2023)               |
| Ethylamine-modified activated carbon                          | CPA        | 490.0                              | pH = 7, T = 35 °C        | Ali et al. (2019)               |
| Graphene oxide-Fe <sub>3</sub> O <sub>4</sub>                 | CPA        | 472.0                              | pH = 10, T = 25 °C       | Li et al. (2017)                |
| Granular activated carbon                                     | CPA        | 199.3                              | pH = 9, T = 25 °C        | Cavazos-Cuello et al. (2023)    |
| <b>Bentonite clay</b>                                         | <b>CPA</b> | <b>159.8</b>                       | <b>pH = 7, T = 25 °C</b> | <b>This work</b>                |
| Agronomic waste material                                      | CPA        | 72.4                               | pH = 8, T = 25 °C        | Sharma et al. (2018)            |
| Zeolite                                                       | CPA        | 1.4                                | pH = 6, T = 25 °C        | Al-rimawi et al. (2019)         |

### 5.3.6 Effect of solution pH, ionic strength, and temperature on adsorption capacity of bentonite towards TMP and CPA

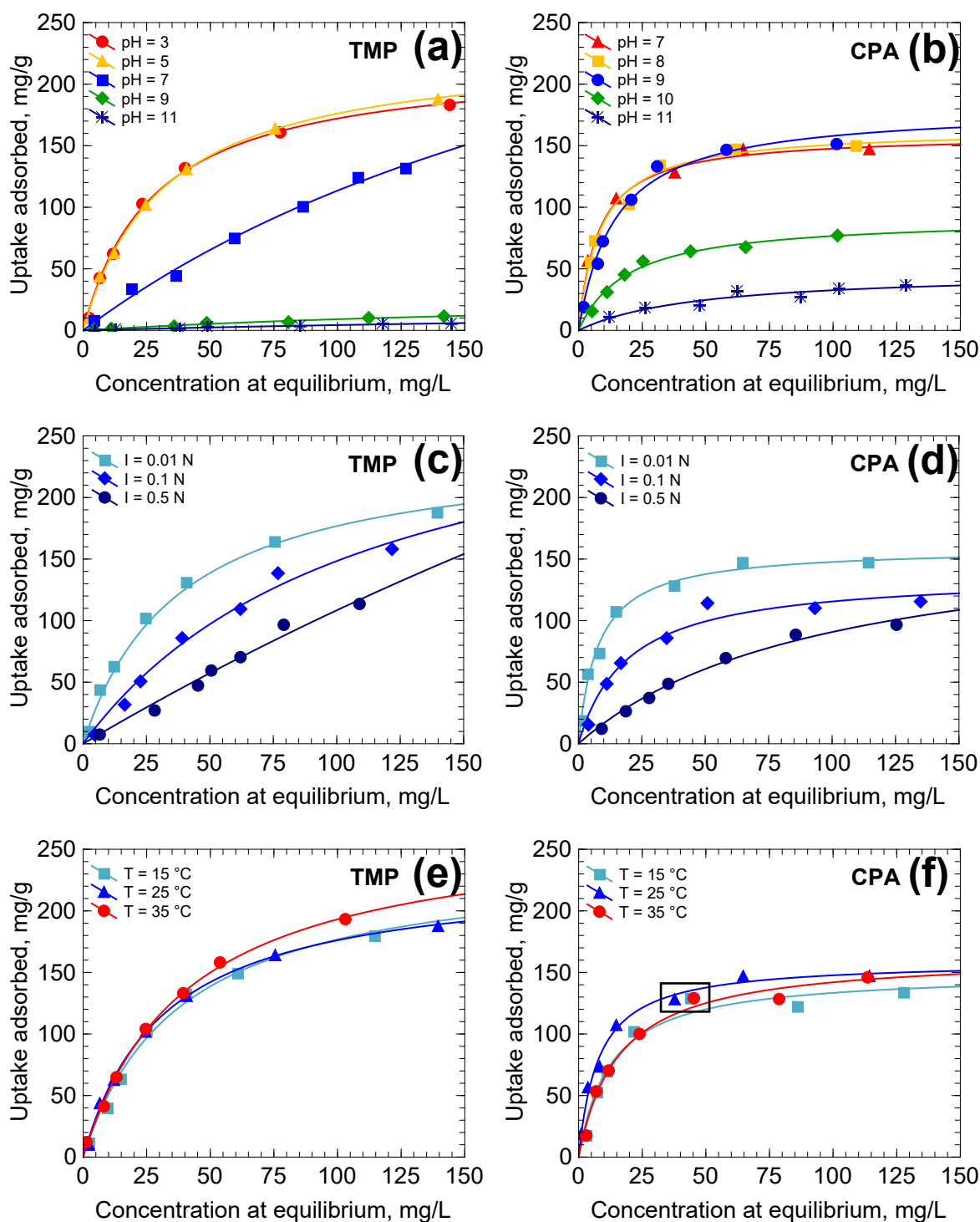
Figures 5.9 (a) and 5.9 (b) exhibits the effect of solution pH on the adsorption isotherms of TMP and CPA on Bent at I = 0.01 N and T = 25 °C. In Figure 5.9 (a), it is shown that the capacity of Bent to adsorb TMP decreased as the solution pH increased. It was observed that at pH 3 and 5, there was no significant effect on the adsorption

capacity since the adsorption isotherms were quite similar. However, at pH 7, the adsorption capacity diminished significantly, while at pH 9 and 11, the uptake of TMP onto Bent was minimal. The uptake of TMP adsorbed on Bent at an equilibrium concentration of 130 mg/L was 181.4, 186.6, 137.1, 10.8, and 5.3 mg/g for pH values of 3, 5, 7, 9, and 11, respectively.

The variation in the capacity of Bent toward TMP adsorption can be explained by the chemical speciation of TMP and the surface charge of Bent. At pH 3 and 5, the ionic charge of TMP is positive ( $\text{TMP}^+$ ), while the surface charge of Bent is negative, leading to a high adsorption capacity due to electrostatic attraction between  $\text{TMP}^+$  and the negatively charged surface of Bent. On the other hand, at pH 7, two chemical species of TMP are present in equal molar proportions, the cationic  $\text{TMP}^+$  and the neutral  $\text{TMP}^0$ , and the reduction in uptake adsorbed is related to the absence of electrostatic interactions between  $\text{TMP}^0$  species and the surface of Bent. Finally, at pH 9 and 11, the predominant chemical species is  $\text{TMP}^0$ , and the uptake adsorbed of TMP is close to zero, as the  $\text{TMP}^0$  species does not adsorb on the surface of Bent.

Figure 5.9 (b) depicts the adsorption isotherms of CPA on Bent at  $I = 0.01\text{ N}$  and  $T = 25\text{ }^\circ\text{C}$ . Experiments were performed at pH values above 7 due to the degradation of CPA in acidic media observed in the absorption spectra. The adsorption isotherms of CPA on Bent show a similar behavior to that of TMP. At pH 7, 8, and 9, there were no significant changes in adsorption capacity; however, at pH 10 and 11, the adsorption capacity decreased considerably. For example, at an equilibrium concentration of 110 mg/L, the uptake adsorbed of CPA onto Bent at pH 7, 8, 9, 10 and 11 was 148.6, 151.9, 159.8, 77.8 and 33.6 mg/g, respectively, indicating that the adsorption capacity reduced by a factor of 4.7 as the pH solution increased from 9 to 11.

The adsorption of CPA on Bent can be explained as follows. At pH 7, 8, and 9, the cationic species of CPA ( $\text{CPA}^+$ ) prevails, and thus, the maximum uptake of CPA adsorbed is associated with the electrostatic attraction between  $\text{CPA}^+$  and the negatively charged Bent surface. Conversely, the decrease in adsorption capacity at pH 10 and 11 is attributed to the existing  $\text{CPA}^0$  species and the occurrence of non-attractive interactions with Bent.



**Figure 5.9.** Effect of solution pH (a, b), ionic strength (c, d) and temperature (e, f) on adsorption isotherms of TMP and CPA onto Bent. The lines represent the Langmuir adsorption isotherm.

The impact of the solution ionic strength on the adsorption capacity of Bent for TMP and CPA at  $T = 25\text{ }^{\circ}\text{C}$  is illustrated in Figures 5.9 (c) and 5.9 (d). Experimental data were obtained at pH 5 and 7 for TMP and CPA, respectively. The adsorption isotherms showed that for both pharmaceuticals, the uptake of TMP and CPA adsorbed on Bent diminishes significantly by increasing the ionic strength of the solution. At an equilibrium concentration of 130 mg/L for TMP, the adsorption capacity of Bent diminished of about 1.1 times as the ionic strength increased from 0.01 to 0.1 N, and by at least 1.36 times as the ionic strength augmented from 0.01 to 0.5 N. In the case of CPA and at an equilibrium concentration of 110 mg/L, the uptake of CPA adsorbed on Bent lessened by 1.57 times as the ionic strength raised from 0.01 to 0.5 N.

This effect can be attributed to a competitive phenomenon among  $\text{Na}^+$  cations and  $\text{TMP}^+$  and  $\text{CPA}^+$  cations for adsorption on the negatively charged sites of the surface of Bent, which also underlines the significant role of electrostatic attractions in the adsorption mechanism of TMP and CPA on Bent.

Figures 5.9 (e) and 5.9 (f) displays the effect of solution temperature on the adsorption of TMP and CPA onto Bent at 15, 25, and 35  $^{\circ}\text{C}$ . Figure 5.9 (e) shows that the solution temperature has a relatively minor influence on the capacity of Bent toward TMP adsorption. Notably, the adsorption capacity remained relatively stable as the temperature increased from 15 to 25  $^{\circ}\text{C}$ , exhibiting a slight increase at 35  $^{\circ}\text{C}$  and for higher TMP concentrations. As for the adsorption isotherms of CPA, the solution temperature had a minor effect on the adsorption capacity of Bent to adsorb CPA, Figure 5.9 (f). The maximum uptake adsorbed of CPA onto Bent was observed at 25  $^{\circ}\text{C}$ , reaching 149.5 mg/g at an equilibrium concentration of 110 mg/L. At 15 and 35  $^{\circ}\text{C}$ , the uptake of CPA was 134.7 and 143.7 mg/g, respectively. It is important to note that there was a 1.2-fold increase in adsorption capacity from 15 to 25  $^{\circ}\text{C}$ , but unexpectedly, it decreased slightly as the temperature diminished from 25 to 35  $^{\circ}\text{C}$ . In addition, in the fifth set of experimental data points shown as a black square in the figure, corresponding to experiments with an initial concentration of 200 mg/L of CPA, the uptake of CPA adsorbed was around 129 mg/g for the three temperatures studied. Even though these results are inconclusive regarding whether the adsorption systems



are endothermic or exothermic, they suggest that temperature does not play a significant role in the adsorption of TMP and CPA onto Bent.

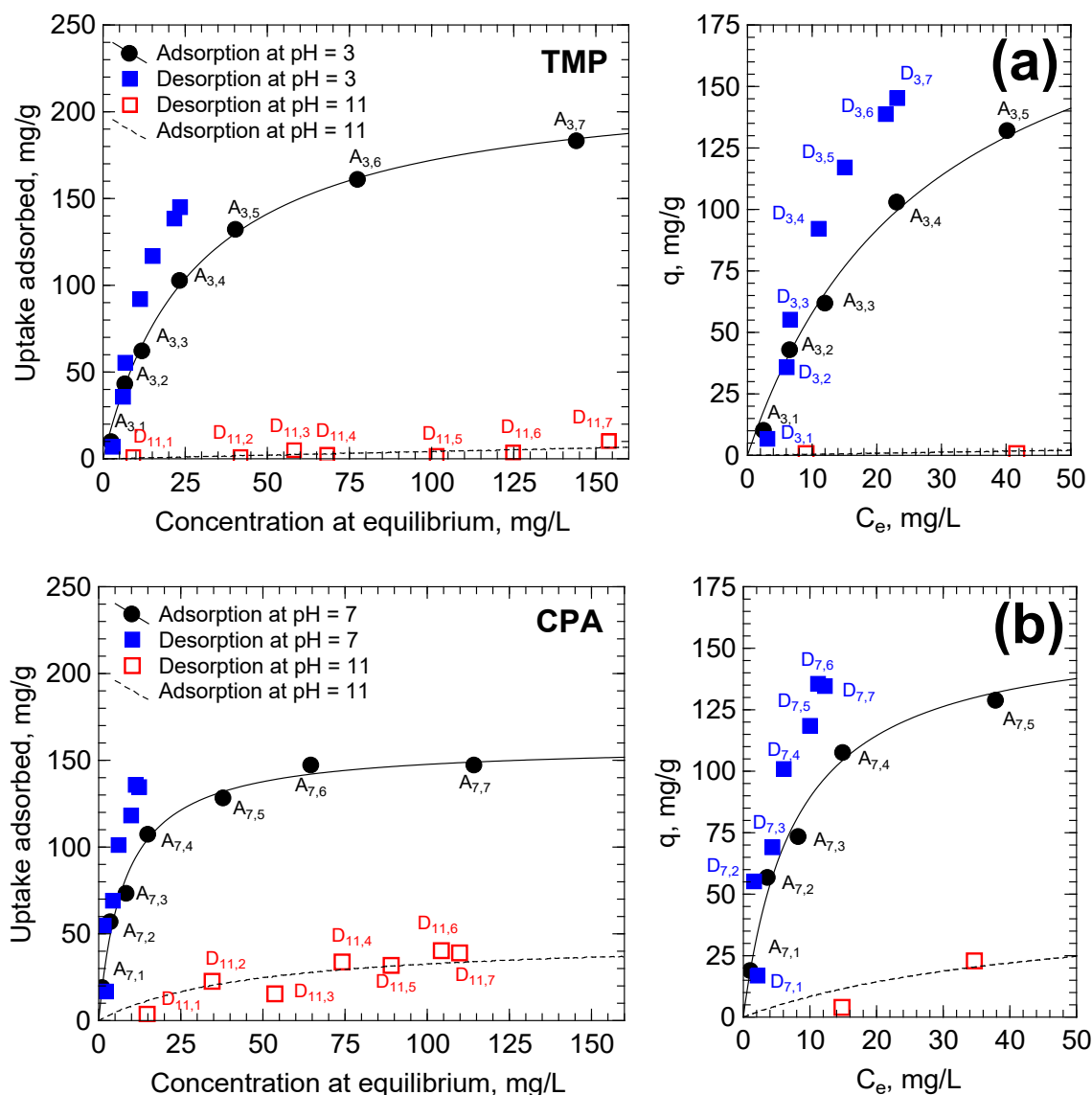
### **5.3.7 Reversibility studies of adsorption of TMP and CPA on bentonite**

A study was conducted to assess the reversibility of TMP and CPA adsorption on Bent by performing adsorption equilibrium experiments at the pH corresponding to the maximum adsorption capacity, followed by desorption at the pH of the minimum adsorption capacity. Figure 5.10 displays the experimental data for TMP and CPA adsorption on Bent, indicated by black markers. Here, each data point is labeled with the letter “A” followed by the pH value and the experiment number, e.g., “A<sub>3,6</sub>” refers to the sixth adsorption experiment conducted at pH 3. In this figure, the experimental data of the desorption equilibrium are represented by blue and red markers and labeled with the letter “D”, followed by the pH value and the experiment number, e.g., “D<sub>11,6</sub>” represents the sixth desorption experiment carried out at pH 11.

Tables 5.7 and 5.8 list the values of  $q_o$ ,  $q_d$ ,  $q_{d,rev}$  and %Des. These values were determined using Equations (4.2, 4.3 and 4.14). The estimation of  $q_{d,rev}$  was accomplished by simultaneously solving the mass balance equation for desorption, as expressed in Equation (4.3), and the Langmuir adsorption isotherm model corresponding to the pH used in the desorption experiments.

It is worth mentioning that an adsorption system is considered reversible if the experimental desorption data align with the adsorption isotherm corresponding to the pH at which the contaminant was desorbed, revealing that weak physical interactions primarily drive the adsorption. Conversely, if the desorption equilibrium data do not match the adsorption isotherm at the pH at which the contaminant was desorbed, the adsorption is considered irreversible, indicating a significant contribution of chemical interactions. As shown in Figure 5.10 (a), the experimental desorption data at pH 3 are situated above the adsorption isotherm at the same pH, indicating an irreversible behavior. Conversely, in the desorption at pH 11, the data resulted close to the adsorption isotherm at pH 11, revealing a reversible behavior. As detailed in Table 5.7, desorption percentages range from 57.1 to 100 % at pH 3 and from 91.9 to 100 % at

pH 11. Figure 5.10 (b) illustrates similar behavior for the adsorption and desorption of CPA. Desorption experiments at pH 7 showed desorption data above the adsorption isotherm at pH 7, whilst desorption experiments at pH 11 closely aligned with the adsorption isotherm at pH 11, indicating the occurrence of chemical and physical interactions in the adsorption mechanism of CPA onto Bent. Desorption percentages varied from 40.2 to 100 % at pH 7, and from 93.6 to 100 % at pH 11 (Table 5.8).



**Figure 5.10.** Adsorption isotherm of TMP (a) and CPA (b) on Bent at  $T = 25\text{ }^{\circ}\text{C}$ .

The lines represent the Langmuir adsorption isotherm.

**Table 5.7.** Desorption percentages of the adsorption-desorption experiments of TMP on Bent at T = 25 °C. Adsorption was performed at pH 3, while desorption was carried out at pH 3 and 11.

| Exp. No. | q <sub>o</sub> (mg/g) | Desorption a pH = 3   |                           |      | Desorption a pH = 11  |                           |      |
|----------|-----------------------|-----------------------|---------------------------|------|-----------------------|---------------------------|------|
|          |                       | q <sub>d</sub> (mg/g) | q <sub>d,rev</sub> (mg/g) | %Des | q <sub>d</sub> (mg/g) | q <sub>d,rev</sub> (mg/g) | %Des |
| 1        | 10.1                  | 7.1                   | 8.9                       | ~100 | 1.2                   | 0.4                       | 91.9 |
| 2        | 43.0                  | 36.0                  | 36.4                      | ~100 | 1.1                   | 1.7                       | ~100 |
| 3        | 62.0                  | 55.5                  | 53.2                      | 73.5 | 5.1                   | 2.6                       | 95.7 |
| 4        | 103.1                 | 92.2                  | 85.5                      | 61.7 | 2.1                   | 4.2                       | ~100 |
| 5        | 132.1                 | 117.4                 | 106.4                     | 57.1 | 3.8                   | 5.2                       | ~100 |
| 6        | 161.2                 | 139.1                 | 123.9                     | 59.3 | 10.3                  | 6.6                       | 97.6 |
| 7        | 183.1                 | 145.6                 | 124.3                     | 63.7 | 2.6                   | 4.3                       | 100  |

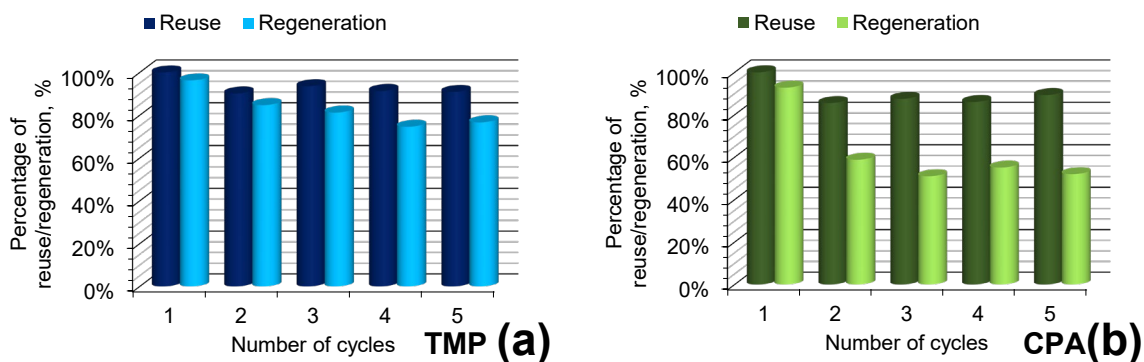
**Table 5.8.** Desorption percentages of the adsorption-desorption experiments of CPA on Bent at T = 25 °C. Adsorption was performed at pH 7, while desorption was carried out at pH 7 and 11.

| Exp. No. | q <sub>o</sub> (mg/g) | Desorption at pH = 7  |                           |      | Desorption at pH = 11 |                           |      |
|----------|-----------------------|-----------------------|---------------------------|------|-----------------------|---------------------------|------|
|          |                       | q <sub>d</sub> (mg/g) | q <sub>d,rev</sub> (mg/g) | %Des | q <sub>d</sub> (mg/g) | q <sub>d,rev</sub> (mg/g) | %Des |
| 1        | 19.1                  | 17.1                  | 18.2                      | ~100 | 1.1                   | 0.4                       | ~100 |
| 2        | 56.9                  | 55.4                  | 53.0                      | 40.2 | 1.1                   | 1.7                       | 93.6 |
| 3        | 73.4                  | 69.2                  | 67.8                      | 74.3 | 4.8                   | 2.4                       | ~100 |
| 4        | 107.4                 | 101.3                 | 95.4                      | 51.1 | 2.0                   | 4.0                       | 94.3 |
| 5        | 128.7                 | 118.7                 | 110.4                     | 54.2 | 3.6                   | 4.9                       | 99.0 |
| 6        | 147.2                 | 135.9                 | 121.2                     | 43.2 | 9.8                   | 6.2                       | 94.2 |
| 7        | 147.1                 | 134.8                 | 121.1                     | 47.2 | 2.5                   | 4.0                       | 95.4 |

### 5.3.8 Regeneration and reuse cycles of bentonite

The reuse of Bent for the adsorption of TMP and CPA was assessed through a series of regeneration and reuse cycles, as is depicted in Figure 5.11. The adsorption capacity of Bent for TMP and CPA was 131.1 and 128.6 mg/g, respectively, which corresponds to 100 % of adsorption in the first cycle. As is shown in this figure, Bent

can be effectively reused for at least 5 cycles while maintaining adsorption percentages for TMP and CPA above 85 %. It should be noted that Bent was not fully regenerated in each cycle. Moreover, the regeneration percentages of Bent after adsorption of TMP and CPA gradually decreased after 5 reuse cycles, from 96.6 to 76.7 % for TMP and from 92.8 to 52.0 % for CPA. These results suggest that although some TMP and CPA molecules remain adsorbed on the surface of Bent after regeneration, they do not hinder the adsorption of more molecules because most of them are desorbed in the regeneration process, which is consistent with the existence of chemical and physical interactions in the adsorption mechanisms of TMP and CPA on Bent.



**Figure 5.11.** Reuse cycles and regeneration of Bent for the adsorption of TMP (a) and CPA (b).

### 5.3.9 Adsorption isotherms in wastewater samples

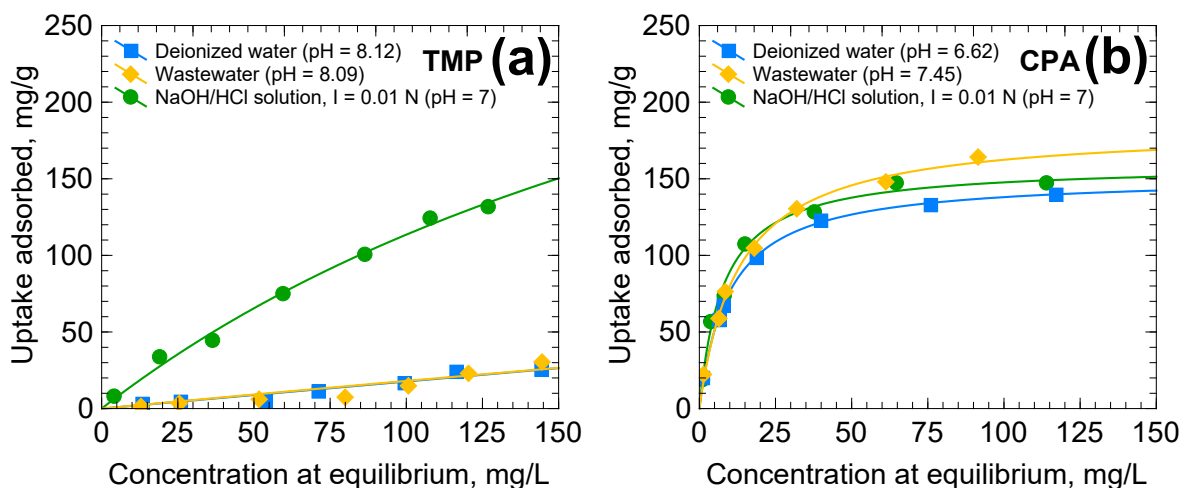
The adsorption of TMP and CPA on Bent was investigated in samples of deionized water, wastewater, and a solution of constant ionic strength prepared from 0.01 N NaOH and HCl solutions. The pH of the solution was not controlled in the deionized water and wastewater samples, while in the constant ionic strength solution, the pH was maintained at a value of 7 throughout the experiment. The wastewater was provided by the Agua Tratada del Potosí S.A. de C.V. plant, located in San Luis Potosi, Mexico, and was collected at the outlet of the second treatment stage. The physicochemical parameters of the wastewater sample before the adsorption of TMP and CPA on Bent are detailed in Table 5.9.

**Table 5.9.** Physicochemical characterization of wastewater before and after adsorption of TMP and CPA on Bent.

| Physicochemical parameter                           | Before adsorption | After adsorption |       |
|-----------------------------------------------------|-------------------|------------------|-------|
|                                                     |                   | TMP              | CPA   |
| Solution pH                                         | 8.03              | 8.09             | 7.45  |
| Electrical conductivity ( $\mu\text{S}/\text{cm}$ ) | 843               | 821              | 807   |
| Total dissolved solids (mg/L)                       | 425               | 400              | 403   |
| Alkalinity (m $\text{CaCO}_3/\text{L}$ )            | 280               | 263              | 260   |
| Bicarbonates (mg/L)                                 | 169.4             | 161.8            | 157.3 |
| Total hardness (m $\text{CaCO}_3/\text{L}$ )        | 79.9              | 60.8             | 59.9  |
| Chlorides (mg/L)                                    | 135.5             | 126.5            | 125.5 |
| Sulfates (mg/L)                                     | 91                | 83               | 81    |
| Calcium (mg/L)                                      | 32.2              | 32.2             | 32.4  |
| Magnesium (mg/L)                                    | 2.0               | 2.2              | 3.8   |
| Potassium (mg/L)                                    | 19.6              | 19.5             | 18.9  |
| Sodium (mg/L)                                       | 108.0             | 105.0            | 93.8  |

Figure 5.12 depicts the adsorption isotherms of TMP and CPA on Bent in three different aqueous matrices: deionized water, wastewater, and NaOH/HCl 0.01 N aqueous solution with constant ionic strength. The pH of the solution at the end of the adsorption is reported in the same figure. Figure 5.12 (a) shows that Bent exhibited high adsorption capacity for TMP in the constant ionic strength solution, but this capacity decreased significantly in deionized water and wastewater samples. For example, at an equilibrium concentration of 130 mg/L, the adsorption capacities were 137.1, 23.3 and 23.0 mg/g for the constant ionic strength solution, deionized water, and wastewater, respectively. On the other hand, the adsorption isotherms of CPA on Bent (Figure 5.12 (b)) revealed that Bent has a high adsorption capacity to adsorb CPA regardless of the type of aqueous matrix. For example, at an equilibrium concentration of 110 mg/L, the adsorbed amounts were 148.6, 139.9 and 168.4 mg/g for the constant ionic strength solution, deionized water, and wastewater, respectively.

Following the adsorption experiment of TMP and CPA on Bent, wastewater samples were analyzed, and the results of physicochemical parameters are presented in Table 5.9. Variations in the solution pH were observed after the adsorption of TMP and CPA on Bent. In the sample corresponding to CPA adsorption, the solution pH decreased to 7.45, whereas in the sample related to TMP adsorption, the pH remained nearly constant at 8.09. Additionally, in deionized water samples, the solution pH was 8.12 and 6.62 for TMP and CPA adsorption, respectively. It was also noted that the concentration of all physiochemical parameters decreased significantly, while the concentration of cations  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ , and  $\text{Na}^{+}$  showed slight variation.



**Figure 5.12.** Adsorption isotherms of TMP (a) and CPA (b) on Bent in deionized water, wastewater, and NaOH/HCl 0.01 N constant ionic strength solution at  $T = 25^{\circ}\text{C}$ .

The findings of this study reveal that Bent significantly improves the quality of wastewater after the adsorption process of TMP and CPA. It was also observed that the solution pH considerably affects the adsorption capacity of TMP and CPA, while other physicochemical parameters have little effect on adsorption capacity. The drastic decrease in the adsorption capacity for TMP in deionized water and wastewater samples is attributed to the fact that, at pH values above 8, as depicted in Figure 5.1, TMP exists in its neutral form as  $\text{TMP}^0$  and cannot be electrostatically attracted to the negative surface of Bent. On the other hand, the slight variation in the adsorption

capacity of CPA is because, at pH values between 6.62 and 7.45, CPA exists as  $\text{CPA}^+$  and can be adsorbed on the negative surface of Bent through electrostatic attractions.

## **5.4 Conclusions**

The characterization of Bent samples saturated with varying the uptakes adsorbed of TMP and CPA revealed the effect of the chemical, structural, textural, and swelling properties of Bent on the adsorption of these pharmaceuticals. It was found that adsorption of the molecules occurred on the external surface and within the interlayer spacing of Bent, predominantly driven by cation exchange and electrostatic attractions. Furthermore, the molecular size of the pharmaceuticals and the swelling capacity of Bent played an essential role in the adsorption processes since the  $d_{001}$  values increased for higher TMP uptakes adsorbed but remained unchanged by raising the uptake of CPA adsorbed. This suggests that TMP intercalates parallel across its XZ transversal area, whereas CPA exhibits an orientation over its XY transversal section.

The pH of the solution strongly influenced the capacity of Bent to adsorb TMP and CPA since the chemical speciation of pharmaceuticals and the surface charge of Bent are pH dependent. The maximum uptake of TMP and CPA adsorbed was attained at pH 5 and 7, respectively, where the chemical species  $\text{TMP}^+$  and  $\text{CPA}^+$  predominated, and by increasing the pH of the solution, the adsorption capacity of Bent diminished. Besides, the studies of the ionic strength of the solution highlighted the role of electrostatic attractions in the adsorption mechanism. Conversely, solution temperature showed no significant effect on the adsorption capacity of Bent to adsorb TMP and CPA. The reversibility assays indicated that the adsorption of TMP and CPA on Bent is controlled by physical and chemical mechanisms. Lastly, the reuse experiments demonstrated that Bent can be used for at least 5 cycles while maintaining adsorption percentages above 85 %. Finally, it was found that bentonite enhances the quality of wastewater following the adsorption of TMP and CPA. Furthermore, it was observed that the pH levels of the solution play a significant role in affecting the adsorption capacity of TMP and CPA. Interestingly, the study indicates that variations in

physicochemical parameters and the presence of secondary species do not seem to impact the adsorption capacity of TMP and CPA.



# CHAPTER

# 6

**MODELING ADSORPTION RATE  
OF TRIMETHOPRIM,  
TETRACYCLINE AND  
CHLORPHENAMINE FROM  
AQUEOUS SOLUTIONS ONTO  
NATURAL BENTONITE CLAY.  
ELUCIDATING MASS TRANSFER  
MECHANISMS**

## **6.1 Introduction**

Pharmaceutical compounds are potentially toxic emerging contaminants whose presence in water systems is of significant environmental concern because they can harm the health of both humans and animals, as well as the sustainability of the environment (Khan et al., 2020; Shahid et al., 2021). These pharmaceutical compounds include different substances such as non-steroidal anti-inflammatories, antihistamines, antibiotics, antiepileptics,  $\beta$ -blockers, and antidepressants, which are being continuously released into surface and groundwater systems through hospital, industrial, and municipal effluents and are detected in a wide range of levels in the order of ng/L to  $\mu$ g/L (Chaturvedi et al., 2021; Bexfield et al., 2019; Zhou et al., 2019). For this reason, it is crucial to diminish the concentrations of emerging pollutants in water resources.

Lately, there has been increased attention to employing natural clays to remove pharmaceutical compounds from water by adsorption due to their chemical, structural and swelling properties, surface area and cation exchange capacity. In this regard, some studies have been carried out on the adsorption equilibrium of different pharmaceuticals including sulfamethoxazole, metronidazole and spiramycin on palygorskite (Habibi et al., 2018; Hernández et al., 2023); ciprofloxacin, amoxicillin, trimethoprim and sulfamethoxazole on montmorillonite (Antonelli et al., 2020; De Oliveira et al., 2018; Gulen and Demircivi, 2020); tetracycline on stevensite (Fernández et al., 2018), venlafaxine on vermiculite (Silva et al., 2018) and oxytetracycline on halloysite (Ramanayaka et al., 2020). Recently, Ortiz-Ramos et al. (2022) investigated the adsorption of tetracycline on different natural clays having distinct structural characteristics, and bentonite presented the highest adsorption capacity (283.5 mg/g at pH = 3) because of its structural properties, swelling and nature of the interlaminar cations.

The design of fixed bed adsorbers and their large-scale operation requires knowledge of the capacity of the material for adsorbing the pollutant and the adsorption rate of the pollutant. Hence, understanding the mass transfer mechanisms governing

the overall adsorption rate of organic compounds on natural clays is crucial and has yet to be investigated thoroughly.

The overall adsorption rate on porous solids depends on three simultaneously occurring stages (Leyva-Ramos and Geankoplis, 1985, 1994). These stages include i) external mass transport, ii) intraparticle diffusion and iii) adsorption rate on an adsorption site. Kinetic and diffusional models can be applied to interpret the experimental adsorption rate data. The rate-controlling step in kinetic models is the adsorption rate on the active site on the adsorbent surface, which neglects external mass transfer and intraparticle diffusion. The main drawback of the kinetic models is that the porous structure of the adsorbent is not considered.

Diffusional models consider the adsorbent porous structure and assume that the adsorption kinetics is affected by the stages i) external mass transport and ii) intraparticle diffusion. Besides, diffusion within the pores may occur by surface diffusion, pore volume diffusion, or combining the two mechanisms. The diffusional models have been applied to satisfactorily interpret the adsorption rate of inorganic and organic pollutants in several porous solids, such as granular activated carbon, activated carbon fiber, organoclays, bone char and biosorbents, among others.

Weber and Morris (1963) proposed a simplified intraparticle diffusion model (IDM) that has been applied to adsorbents with a very well-developed porous structure (Bui et al., 2013; Liu et al., 2017; Sahin et al., 2020; Sun et al., 2012; Zhang et al., 2011). Recently, some authors applied the IDM model to analyze the adsorption rate of pharmaceuticals on natural clays. Antonelli et al. (2020) and Gulen and Demircivi (2020) studied the adsorption rate of ciprofloxacin on montmorillonite. They found that the experimental adsorption kinetic data could not be efficiently interpreted using the IDM model and concluded that intraparticle diffusion did not affect the overall adsorption rate. Similar results were found in other works (Çalışkan Salihi et al., 2023; del Mar Orta et al., 2019). In contrast, Wu et al. (2019) interpreted the adsorption kinetics of tetracycline and ciprofloxacin on montmorillonite with the IDM model and determined that intraparticle diffusion governs the overall adsorption rate. Comparable results were reported for the adsorption kinetics of trimethoprim on montmorillonite

(Bekçi et al., 2006). Re-examining the present literature, the results for IDM are contradictory and do not show clear evidence of the mass transport mechanisms affecting the adsorption kinetics of the pharmaceuticals on natural clays. This trend may be ascribed to the fact that the IDM model does not consider the different types of intraparticle diffusion occurring in porous solids and the external mass transfer.

The adsorption of dyes, insecticides, pharmaceutical compounds and polyvinyl alcohol on natural and modified bentonite has been investigated (Ma et al., 2012; Rauf et al., 2012; Vimonses et al., 2009; Wang et al., 2013). The adsorption rate has been analyzed using the kinetic, Weber and Morris and IDM models. However, no work has been reported about interpreting the adsorption rate of organic compounds on bentonite using the diffusional models. Additionally, the intraparticle diffusion mechanisms of organic compounds in the adsorption rate on natural clays have not been thoroughly elucidated, and the contribution of each intraparticle diffusion mechanism has yet to be evaluated.

Previous works have not reported the surface diffusion and pore volume diffusion coefficients of the organic compounds during adsorption on clays. Furthermore, the tortuosity factor has not been evaluated to estimate the pore volume diffusion coefficient of organic compounds in natural clays.

In this sense, it is necessary to develop and implement diffusional models that consider the physicochemical and structural properties of clays, as well as each of the intraparticle diffusion mechanisms. Future work should focus on interpreting the adsorption rate of organic pollutants on natural clays using diffusional models.

In Chapter 6, the adsorption kinetics of three pharmaceutical compounds, trimethoprim (TMP), tetracycline (TC) and chlorphenamine (CPA), on a natural bentonite clay, were investigated, and the mass transport mechanisms governing the adsorption rate were elucidated. Different initial concentrations and stirring speeds were used in procuring the concentration decay curves. Then, they were interpreted using diffusional models governed by intraparticle diffusion or external mass transfer. Finally, the influence of the uptake adsorbed of TMP, TC and CPA at equilibrium upon the surface diffusion and pore volume diffusion coefficients was studied.

## 6.2 Diffusional models

### 6.2.1 External Mass Transport Model (EMTM)

The EMTM is derived by supposing that the solute mass transfer from the water solution to the external surface of the bentonite particle plays a crucial role in governing the adsorption kinetics. In addition, the following assumptions can be considered: i) the solute intraparticle diffusion in the bentonite pores is very fast, so there are no gradients of  $C_A$  and  $q$  inside the bentonite particles, and ii) the adsorption rate on an adsorbing site occurs instantaneously. The subsequent mathematical relationships represent the EMTM model (Leyva-Ramos et al., 2012):

$$V \frac{dC_A}{dt} = -mSk_L(C_A - C_{Ar}|_{r=R}) \quad (6.1)$$

$$\text{IC: } t = 0 \quad C_A = C_{A0} \quad (6.2)$$

$$\frac{m\varepsilon_p}{\rho_p} \frac{dC_{Ar}}{dt} + m \frac{dq}{dt} = mSk_L(C_A - C_{Ar}|_{r=R}) \quad (6.3)$$

$$\text{IC: } t = 0 \quad C_{Ar} = 0 \text{ and } q = 0 \quad (6.4)$$

where  $V$  is the volume of the solution,  $\text{cm}^3$ ;  $C_A$  is the concentration of solute,  $\text{mmol/L}$ ;  $C_{A0}$  is the initial concentration of solute,  $\text{mmol/L}$ ;  $C_{Ar}|_{r=R}$  is the concentration of solute at the external surface of Bent particles,  $\text{mmol/L}$ ;  $t$  is the time,  $\text{min}$ ;  $m$  is the mass of adsorbent,  $\text{g}$ ;  $S$  is the external surface area per unit mass of adsorbent,  $\text{cm}^2/\text{g}$ ;  $k_L$  is the external mass transport coefficient,  $\text{cm/s}$ ;  $R$  is the radius of the adsorbent particle,  $\text{cm}$ ;  $r$  is the radial distance,  $\text{cm}$ ;  $\varepsilon_p$  is the void fraction of Bent,  $\rho_p$  is the apparent density of Bent,  $\text{g/cm}^3$ ;  $q$  is the mass of solute adsorbed per unit mass of adsorbent,  $\text{mmol/kg}$ .

Equation (6.1) describes the mass balance of solute A in an aqueous solution, while Equation (6.3) expresses the mass balance of solute A in the adsorbent particles. The parameter  $k_L$  is the external mass transfer coefficient, and the initial conditions (IC) are represented by Equations (6.2) and (6.4).

### 6.2.2 Pore Volume and Surface Diffusion Model (PVSDM)

The Pore Volume and Surface Diffusion Model (PVSDM) was advanced by Leyva-Ramos and Geankoplis (1985) and is dependent on the succeeding

suppositions: i) mass transfer from the solution to the external surface of bentonite is described using an external mass transport coefficient,  $k_L$ ; ii) the intraparticle diffusion within the bentonite pores may happen through pore volume diffusion, surface diffusion, or both of them; iii) the adsorption rate of solute A onto the bentonite active sites is instantaneous. The following equations describe the PVSDM model:

$$V \frac{dC_A}{dt} = -mS k_L (C_A - C_{Ar}|_{r=R}) \quad (6.5)$$

$$\text{IC: } t = 0 \quad C_A = C_{A0} \quad (6.6)$$

$$\epsilon_p \frac{\partial C_{Ar}}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{e,p} \frac{\partial C_{Ar}}{\partial r} + D_{e,s} \rho_p \frac{\partial q}{\partial r} \right) \right] \quad (6.7)$$

$$\text{IC: } t = 0 \quad C_{Ar} = 0 \quad 0 \leq r \leq R \quad (6.8)$$

$$\text{BC: } \left. \frac{\partial C_{Ar}}{\partial r} \right|_{r=0} = 0 \quad (6.9)$$

$$\text{BC: } D_{e,p} \left. \frac{\partial C_{Ar}}{\partial r} \right|_{r=R} + D_{e,s} \rho_p \left. \frac{\partial q}{\partial r} \right|_{r=R} = k_L (C_A - C_{Ar}|_{r=R}) \quad (6.10)$$

where  $C_{Ar}$  is the concentration of solute inside the particle at distance  $r$ , mmol/L;  $D_{e,p}$  is the effective pore volume diffusion coefficient,  $\text{cm}^2/\text{s}$ ;  $D_{e,s}$  is the surface diffusion coefficient,  $\text{cm}^2/\text{s}$ .

A differential mass balance for solute A was accomplished in a spherical element of Bent particle, yielding Equation (6.7). The parameters  $k_L$ ,  $D_{e,p}$  and  $D_{e,s}$  represent the mass transfer, pore volume diffusion and surface diffusion coefficients, respectively. The PVSDM model can become the pore volume diffusion model (PVDm) when  $D_{e,p} \neq 0$  and  $D_{e,s} = 0$ , or the surface diffusion model (SDM) when  $D_{e,p} = 0$  and  $D_{e,s} \neq 0$ .

In the EMTM and PVSDM models, the adsorption rate on an active site happens instantaneously, leading to a state of local equilibrium amidst the solute concentration in the solution inside bentonite pores and the uptake adsorbed of solute on the pore surface. The equilibrium condition can be expressed by the adsorption isotherm and is denoted by the subsequent Equation (6.11):

$$q = f(C_{Ar}) \quad (6.11)$$

## 6.3 Experimental methodology

### 6.3.1 Materials and characterization

The bentonite (Bent) used in this study is a calcium clay composed mainly of montmorillonite. Its extraction and conditioning techniques are detailed in Chapter 4. The solid density of the Bent particles was quantified using a Helium pycnometer, Micromeritics, AccuPyc 1330. The subsequent mathematical relationships were employed to compute the bulk density, void fraction and external surface of Bent particles:

$$\rho_p = \frac{\rho_s}{1 + V_p \rho_s} \quad (6.12)$$

$$\varepsilon_p = \frac{V_p}{V_p + 1/\rho_s} \quad (6.13)$$

$$S = \frac{3}{R\rho_p} \quad (6.14)$$

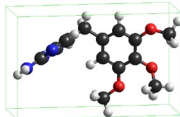
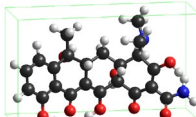
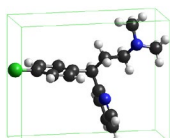
The Bent particles had a solid density of 2.367 g/cm<sup>3</sup>, a bulk density of 1.963 g/cm<sup>3</sup>, a void fraction of 0.17 and an external surface area of 577.1 cm<sup>2</sup>/g.

### 6.3.2 Pharmaceutical compounds

Tetracycline (TC) as an anhydrous base (CAS: 60-54-8), trimethoprim (TMP) (CAS: 738-70-5) and chlorphenamine (CPA) (CAS: 113-92-8) were provided by Merck. Table 6.1 lists their physicochemical properties.

Pharmaceutical compounds in an aqueous solution can donate and accept protons and exhibit different chemical species depending on the solution pH. TMP forms two chemical species, the cationic (TMP<sup>+</sup>) at pH less than 7.16 and the neutral species (TMP<sup>0</sup>) at pH above 7.16. TC can be present in four chemical species. The cationic species of TC (TC<sup>+</sup>) prevails at pH < 3.32, the zwitterionic species (TC<sup>±</sup>) exists in the pH span from 3.32 to 7.78, and at pH > 7.78, the anionic species TC<sup>-</sup> and TC<sup>2-</sup> exist. CPA can form three chemical species: the di-cationic species (CPA<sup>2+</sup>) at pH < 4.0, the cationic one (CPA<sup>+</sup>) in pH range between 4.0 and 9.2 and the neutral species (CPA<sup>0</sup>) at pH above 9.2 (Bekçi et al., 2006; Ortiz-Ramos et al., 2022; Xia et al., 2014).

**Table 6.1.** Physicochemical properties of TMP, TC and CPA.

| Solutes                                  | Family         | Molecular structure <sup>a</sup>                                                  | Molecular size <sup>a</sup><br>(nm) | $D_{AB}^0 \times 10^6$ <sup>b</sup><br>(cm <sup>2</sup> /s) | pK <sub>a</sub> <sup>c</sup> |
|------------------------------------------|----------------|-----------------------------------------------------------------------------------|-------------------------------------|-------------------------------------------------------------|------------------------------|
| Trimethoprim<br>(TMP)<br>M.W. = 290.32   | Antibiotics    |  | X = 1.19<br>Y = 0.74<br>Z = 0.52    | 4.86                                                        | 7.16                         |
| Tetracycline<br>(TC)<br>M.W. = 444.44    | Antibiotics    |  | X = 1.38<br>Y = 0.81<br>Z = 0.69    | 3.81                                                        | 3.32,<br>7.78,<br>9.58       |
| Chlorphenamine<br>(CPA)<br>M.W. = 274.79 | Antihistamines |  | X = 1.11<br>Y = 0.91<br>Z = 0.49    | 5.06                                                        | 4.00,<br>9.20                |

<sup>a</sup> Determined by Density Functional Theory (DFT) using 6-31G B3LYP method.

<sup>b</sup> Molecular diffusion coefficient in dilute solution.

<sup>c</sup> Dissociation constants.

### 6.3.3 Quantification method

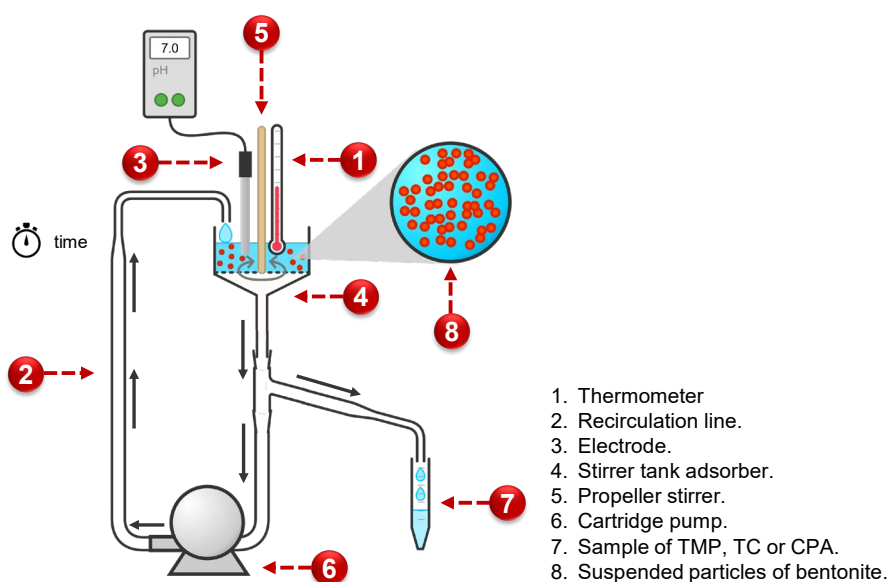
The pharmaceutical concentration in aqueous solutions was appraised in a UV-Vis spectrophotometer, Shimadzu 2600. The calibration curves were prepared employing standard solutions with concentrations varying from 1.35 (0.6 mg/L) to 94.5 (42 mg/L)  $\mu\text{mol/L}$  for TC, 2.06 (0.6 mg/L) to 206.7 (60 mg/L)  $\mu\text{mol/L}$  for TMP and 1.82 (0.5 mg/L) to 191.9 (50 mg/L)  $\mu\text{mol/L}$  for CPA. The TMP, TC and CPA analysis was performed at the wavelengths of 271, 357 and 261 nm, respectively.

### 6.3.4 Kinetic data for adsorbing pharmaceuticals on Bent

The experimental concentration decay data of TMP, TC and CPA adsorbing on Bent were collected in a stirred tank batch adsorber for suspended particles with recirculation (Figure 6.1), described in previous works (Leyva-Ramos et al., 2021; Ocampo-Pérez et al., 2011a, 2011b), and the procedure is described below. Initially, a certain mass of Bent was contacted with 5 mL of a constant ionic strength (0.01 N) solution and specific pH for 30 min. Subsequently, a pharmaceutical solution with a



known initial concentration at a particular pH and a constant ionic strength (0.01 N) was fixed in a 200 mL volumetric flask following the abovementioned procedure. Then, a solution sample (1 mL) was analyzed to quantify the initial concentration ( $C_A = C_{A0}$ ,  $t = 0$ ). The remaining solution was placed in the adsorber, and the stirred motor was turned on at a given stirring speed. Subsequently, the solution containing the suspended Bent particles was added, completing the initial volume to 204 mL, and the timer was started. The concentration of the adsorber solution was monitored periodically for 6 hours, and 13 samples were taken out, ensuring that the volume extracted was under 3.0 % of the adsorber solution. The pharmaceutical concentration in the samples was determined, and the concentration decay curves were obtained over time.



**Figure 6.1.** Stirred tank batch adsorber for suspended particles.

### 6.3.5 Adsorption equilibrium data

The adsorption isotherms of TMP, TC, and CPA on Bent were derived from experimental data of concentration decay curves. These isotherms were constructed by graphically representing  $q_e$  vs.  $C_{Ae}$  at the time equilibrium was reached. The uptake of pharmaceutical compound adsorbed at equilibrium was calculated using the following equation:

$$q_e = \frac{V(C_{A0} - C_{Ae}) \times 1000}{m \times MW_A} \quad (6.15)$$

where  $q_e$  is the uptake of pharmaceutical compound adsorbed at equilibrium, mmol/kg;  $MW_A$  is the molecular weight of solute A.

## 6.4 Results and discussion

### 6.4.1 Adsorption isotherms and effect of operating conditions on adsorption capacity

The equilibrium data for TMP, TC and CPA adsorption on Bent were interpreted using the Freundlich, Langmuir and Radke-Prausnitz adsorption isotherm models, expressed by the Equations (4.9-4.11). The Equation (4.12) was used to calculate the average deviation percentage of each adsorption isotherm.

Table 6.2 lists the best-fit parameters and average percentage deviations. It was ascertained that the experimental data for any of the pharmaceutical compounds could not be satisfactorily interpreted by the Freundlich isotherm because it had the highest average percentage deviations. For the adsorption isotherms of CPA and TC, the Radke-Prausnitz model was equivalent to the Langmuir model because  $\beta = 1$ . However, the Radke-Prausnitz provided the best fitting for the TMP adsorption isotherm since the %D for this isotherm model was the lowest. From the above results, the Radke-Prausnitz model was selected to interpret the TMP, TC and CPA adsorption isotherms.

**Table 6.2.** Isotherm parameters and average percentage deviation of the adsorption isotherms of TMP (pH = 5), TC (pH = 3) and CPA (pH = 11) on Bent at T = 25 °C.

| Solutes | Freundlich                       |     |      | Langmuir                    |               |     | Radke-Prausnitz              |                                           |      |     |
|---------|----------------------------------|-----|------|-----------------------------|---------------|-----|------------------------------|-------------------------------------------|------|-----|
|         | K<br>(mmol <sup>1-1/n</sup> /kg) | n   | %D   | q <sub>m</sub><br>(mmol/kg) | K<br>(L/mmol) | %D  | a×10 <sup>-3</sup><br>(L/kg) | b<br>(L <sup>β</sup> /mmol <sup>β</sup> ) | β    | %D  |
| TMP     | 726.7                            | 4.2 | 7.2  | 637.9                       | 26.1          | 1.7 | 18.866                       | 28.8                                      | 0.96 | 1.0 |
| TC      | 596.9                            | 4.2 | 8.1  | 536.8                       | 23.1          | 1.4 | 12.399                       | 23.1                                      | 1.00 | 1.4 |
| CPA     | 309.5                            | 1.2 | 26.9 | 586.4                       | 0.757         | 5.0 | 0.444                        | 0.757                                     | 1.00 | 5.0 |

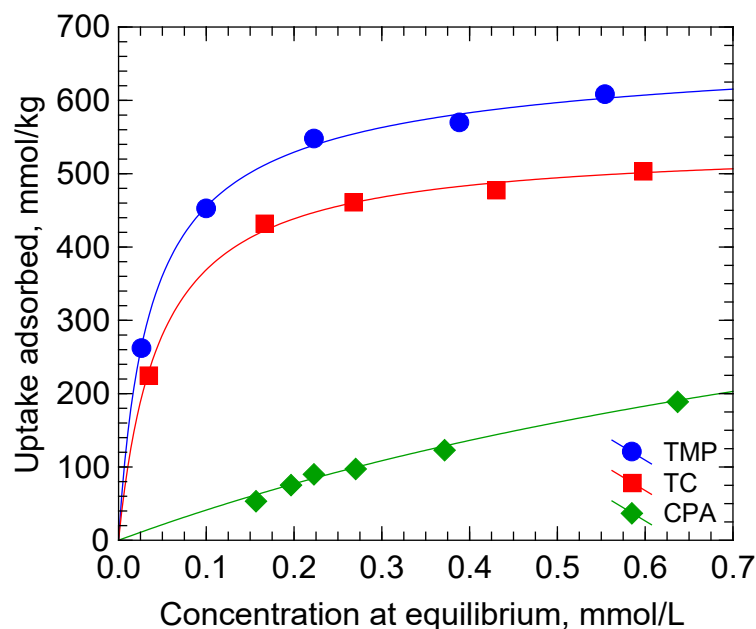
The TMP, TC and CPA adsorption isotherms on Bent are depicted in Figure 6.2 at  $T = 25\text{ }^{\circ}\text{C}$ , and the experimental data for TMP, TC and CPA were obtained at pH 5, pH 3 and pH 11, respectively. The reason for choosing these pH values is to investigate the effect of predominant species of the pharmaceutical compounds on the adsorption rate. The cationic species of  $\text{TC}^+$  and  $\text{TMP}^+$  predominate in aqueous solution at pH of 3 and 5, whereas at  $\text{pH} = 11$ , the predominant species of CPA is the neutral  $\text{CPA}^0$  (Bekçi et al., 2006; Ortiz-Ramos et al., 2022; Xia et al., 2014).

In a previous work about the adsorption of TC on Bent (Ortiz-Ramos et al., 2022), it was found that the maximum adsorption capacity of TC on Bent was at  $\text{pH} = 3$ , and the  $\text{TC}^+$  was mainly adsorbed by electrostatic attractions. In the case of TMP, the results presented in Chapter 5 revealed that the maximum adsorption capacity for TMP was at  $\text{pH} = 5$ , and the predominant species is  $\text{TMP}^+$ . At  $\text{pH} = 11$ , the predominant species of CPA is the neutral  $\text{CPA}^0$ , and the adsorption of CPA is not affected by electrostatic attraction.

As seen in Figure 6.2, Bent presented high adsorption capacities towards TMP and TC but low towards CPA. For an equilibrium concentration of  $0.5\text{ mmol/L}$ , the uptake adsorbed of TMP, TC and CPA were 596.9, 493.6 and  $160.9\text{ mmol/kg}$ , correspondingly. The uptake adsorbed of TMP was 1.21 and 3.71 times higher than that of TC and CPA. The Bent adsorption capacity lessened in the subsequent order:  $\text{TMP} > \text{TC} > \text{CPA}$ .

The zeta potential distribution of the Bent surface was measured in Chapter 4, and the isoelectric point of Bent was  $\text{pH}_{\text{IEP}} < 2$ , so the Bent surface was negatively charged for  $\text{pH} > 2$ . The TMP and TC adsorption on Bent at  $\text{pH} = 5$  and 3 can be explained considering that TC and TMP species in the aqueous solution were cations, and the Bent surface was negatively charged in the pH range studied. Then, the high capacity of Bent to adsorb TC and TMP is due to the electrostatic attraction between the  $\text{TC}^+$  and  $\text{TMP}^+$  cations and the negatively charged surface of Bent. Also, cation exchange may happen between  $\text{TC}^+$  or  $\text{TMP}^+$  and the interchangeable cations located in the interlayer space of Bent, as reported previously on the TC adsorption on various natural clays (Ortiz-Ramos et al., 2022). On the other hand, the low adsorption capacity

towards CPA can be ascribed to the absence of electrostatic interaction because the CPA<sup>0</sup> species in solution at pH 11 is neutral or undissociated. In this case, the adsorption may occur by weak physical interactions such as hydrogen bonding between hydroxyls in the Bent layers and the polar groups of CPA.



**Figure 6.2.** Adsorption isotherms of TMP (pH = 5), TC (pH = 3) and CPA (pH = 11) on Bent at T = 25 °C. The lines represent the Radke-Prausnitz isotherm.

The effect of temperature in the adsorption of TC, TMP and CPA on Bent was reported in Chapters 4 and 5, and the results revealed that the adsorption capacity towards TC raised by incrementing the temperature from 15 to 35 °C. The effect of temperature on the adsorption capacity towards CPA and TMP confirms that the adsorption capacity of Bent towards TMP increases slightly by raising the temperature from 15 to 35 °C. In contrast, the capacity for adsorbing CPA is essentially not affected by temperature. Hence, the adsorption of TC and TMP was endothermic.

#### 6.4.2 Experimental concentration decay curves for TMP, TC and CPA

Table 6.3 presents the working conditions for procuring the concentration decay curves of TMP (Exp. Nos. 1-5), TC (Exp. Nos. 6-10) and CPA (Exp. Nos. 11-15) during

adsorption on Bent at  $T = 25\text{ }^{\circ}\text{C}$ . Five runs were conducted for each pharmaceutical compound, and the experimental conditions were the stirring speed as well as the pharmaceutical initial concentration in the stirred tank batch adsorber.

**Table 6.3.** Mass transport parameters for the adsorption of TMP (pH = 5), TC (pH = 3) and CPA (pH = 11) on Bent at  $T = 25\text{ }^{\circ}\text{C}$ ,  $V = 0.2\text{ L}$  and  $R = 0.0027\text{ cm}$ .

| Exp. No. | Solutes | RPM | $C_{A0}$<br>(mmol/L) | $C_{Ae}$<br>(mmol/L) | $q_e$<br>(mmol/kg) | EMTM model                  |      | PVDM model                                    |          |     | PVSDM model                                   |     |
|----------|---------|-----|----------------------|----------------------|--------------------|-----------------------------|------|-----------------------------------------------|----------|-----|-----------------------------------------------|-----|
|          |         |     |                      |                      |                    | $k_L \times 10^2$<br>(cm/s) | %Dd  | $D_{e,p} \times 10^6$<br>(cm <sup>2</sup> /s) | $\tau_p$ | %Dd | $D_{e,s} \times 10^9$<br>(cm <sup>2</sup> /s) | %Dd |
| 1        | TMP     | 450 | 0.16                 | 0.03                 | 261.8              | 2.97                        | 18.5 | 11.22                                         | 0.07     | 8.6 | 0.89                                          | 9.2 |
| 2        |         | 450 | 0.33                 | 0.10                 | 452.5              | 1.76                        | 8.9  | 14.29                                         | 0.06     | 4.7 | 2.20                                          | 3.6 |
| 3        |         | 450 | 0.50                 | 0.22                 | 547.4              | 1.72                        | 3.6  | 14.59                                         | 0.06     | 2.9 | 4.06                                          | 2.5 |
| 4        |         | 450 | 0.67                 | 0.39                 | 570.0              | 1.17                        | 2.7  | 7.71                                          | 0.11     | 1.5 | 3.00                                          | 1.8 |
| 5        |         | 600 | 0.50                 | 0.23                 | 523.7              | 1.92                        | 3.1  | 18.0                                          | 0.05     | 2.2 | 4.06                                          | 3.9 |
| 6        | TC      | 450 | 0.15                 | 0.03                 | 225.7              | 1.11                        | 23.2 | 1.25                                          | 0.52     | 3.0 | 0.14                                          | 2.6 |
| 7        |         | 450 | 0.38                 | 0.16                 | 431.8              | 0.77                        | 9.3  | 0.81                                          | 0.80     | 2.6 | 0.29                                          | 2.5 |
| 8        |         | 450 | 0.50                 | 0.27                 | 461.4              | 1.02                        | 5.4  | 0.69                                          | 0.94     | 2.3 | 0.34                                          | 2.0 |
| 9        |         | 450 | 0.67                 | 0.43                 | 477.9              | 0.53                        | 6.1  | 0.40                                          | 1.63     | 2.3 | 0.46                                          | 3.6 |
| 10       |         | 600 | 0.49                 | 0.25                 | 474.3              | 0.95                        | 5.7  | 0.69                                          | 0.95     | 1.8 | 0.35                                          | 1.5 |
| 11       | CPA     | 450 | 0.29                 | 0.16                 | 53.8               | 0.17                        | 15.2 | 0.086                                         | 10.1     | 8.9 | -                                             | -   |
| 12       |         | 450 | 0.38                 | 0.20                 | 74.7               | 0.18                        | 7.4  | 0.090                                         | 9.59     | 1.6 | -                                             | -   |
| 13       |         | 450 | 0.45                 | 0.22                 | 90.6               | 0.22                        | 6.9  | 0.093                                         | 9.26     | 3.4 | -                                             | -   |
| 14       |         | 450 | 0.52                 | 0.27                 | 98.0               | 0.13                        | 7.7  | 0.089                                         | 9.64     | 2.2 | -                                             | -   |
| 15       |         | 600 | 0.51                 | 0.27                 | 95.9               | 0.15                        | 6.4  | 0.090                                         | 9.62     | 2.1 | -                                             | -   |

### 6.4.3 Interpretation of the experimental concentration decay data by the EMTM model

First, the experimental adsorption kinetics data for TMP, TC and CPA on Bent was interpreted by the EMTM model. In this model, the mass transfer of the drug molecules from the solution to the Bent external surface controls the overall adsorption rate. Furthermore, intraparticle diffusion is negligible because it is considered to be very fast. The numerical solution of the EMTM model involves evaluating the mass transfer coefficient,  $k_L$ , which was assessed using the succeeding equation suggested by Furusawa and Smith (1973):

$$\left[ \frac{d(C_A/C_{A0})}{dt} \right]_{t=0} = \frac{-mSk_L}{V} \quad (6.16)$$

The slope of the concentration decay curve at  $t = 0$  corresponds to the left-hand side term of this mathematical relationship and was assessed with the experimental data obtained in the first minute. Table 6.3 lists the  $k_L$  values for TMP, TC, and CPA ranging from  $1.17 \times 10^{-2}$  to  $2.97 \times 10^{-2}$  cm/s,  $0.53 \times 10^{-2}$  to  $1.11 \times 10^{-2}$  cm/s, and  $0.13 \times 10^{-2}$  to  $0.22 \times 10^{-2}$  cm/s, respectively. The estimates of  $k_L$  fall within the ranges reported for stirred tank batch adsorbers, which were employed in studying the adsorption kinetics of organic compounds on organobentonite (Ocampo-Perez et al., 2011a, 2011b).

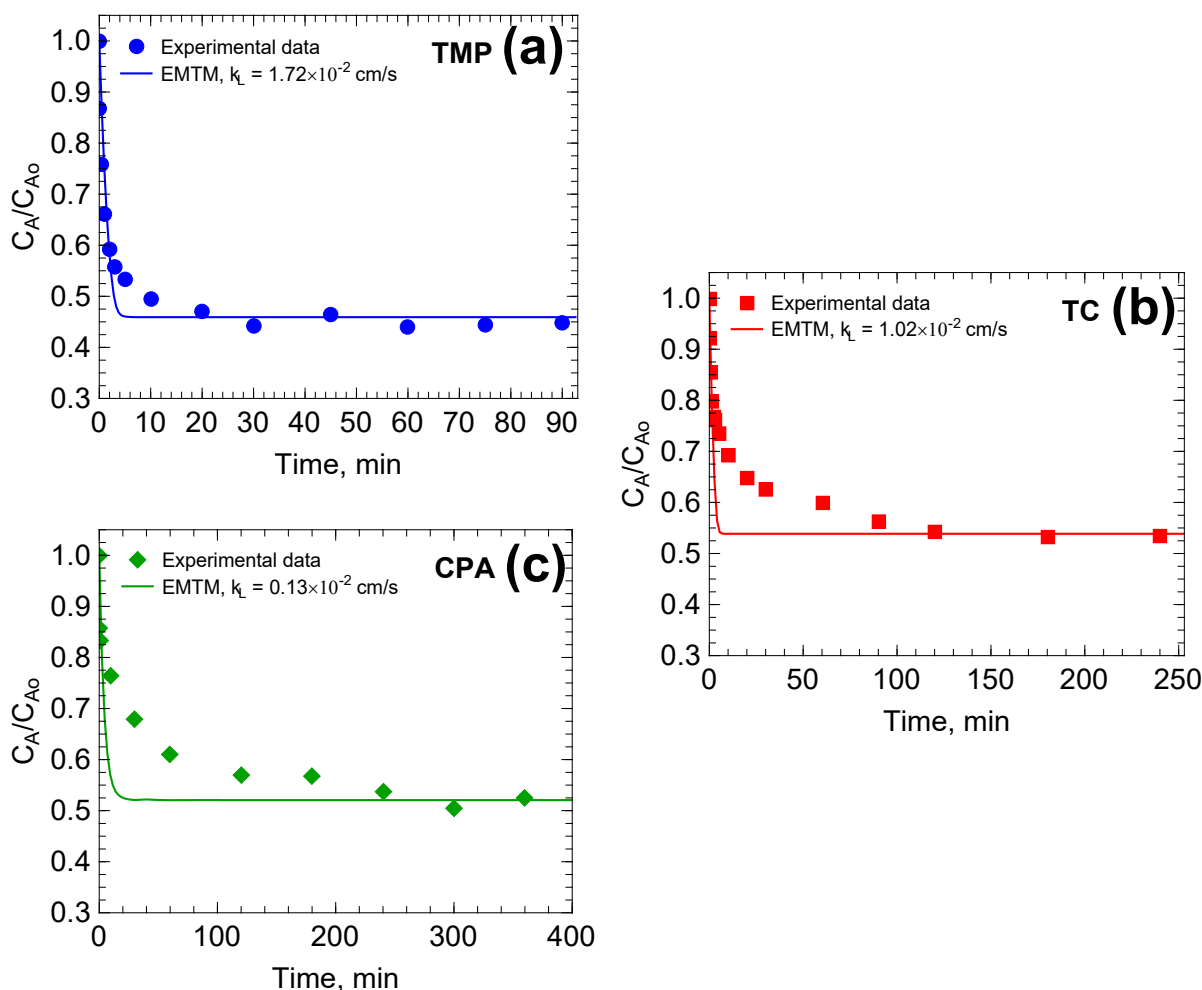
The average percentage deviation for the diffusional models, %Dd, are registered in Table 6.3 and were computed with the subsequent mathematical relationship:

$$\%Dd = \left( \frac{1}{N} \sum_{i=1}^N \left| \frac{(C_A/C_{Ao})_{i,exp} - (C_A/C_{Ao})_{i,pred}}{(C_A/C_{Ao})_{i,exp}} \right| \right) \times 100 \% \quad (6.17)$$

Figure 6.3 illustrates the TMP, TC and CPA concentration decay curves for Exp. Nos. 3, 8 and 14, as well as those predicted with the EMTM model. The experimental data graphed in Figure 6.3 reveal that the TMP, TC and CPA adsorption reached equilibrium at 30, 180 and 300 min, respectively, so the adsorption rate for TMP was 6 and 10 times faster than that of TC and CPA. The EMTM model interpreted the experimental data reasonably within the first 2 min, but predicted that the adsorption equilibrium of TMP, TC and CPA was reached at 4, 7 and 25 min, respectively. Hence, the adsorption rate predicted by the EMTM is 7.5, 17.1 and 12 times faster than the experimental rate, respectively. Similar results were also obtained in Exp. Nos. 1-15, and the average percentage deviation ranged from 2.7 to 23.2 %. These results suggest that the global adsorption rate of TMP, TC and CPA was not controlled by the external mass transfer. The finding that the EMTM model predicted a quicker adsorption rate than the experimental one corroborates that intraparticle diffusion is taking place.

The overall adsorption rate of methylene blue (MB), pentachlorophenol and 1-naphthalene sulfonic acid onto activated carbon fiber, as well as the biosorption rate of MB on wood sawdust, was investigated in previous works (Leyva-Ramos et al., 2012,

2021), and was concluded that the EMTM model predicted adsorption rates much faster than the overall adsorption rate, corroborating that the intraparticle diffusion is crucial in the adsorption rate.



**Figure 6.3.** Concentration decay curves of TMP (a), TC (b) and CPA (c) during adsorption on Bent at  $C_{A0} = 0.5$  mmol/L and  $T = 25$  °C, for Exp. Nos. 3, 8 and 14, respectively. The lines represent the prediction of the EMTM model.

#### 6.4.4 PVDM model interpretation of the experimental concentration decay curves

The PVDM model was employed to analyze the experimental concentration decay curves, and this model assumes that pore volume diffusion controls the overall

adsorption rate ( $D_{e,p} \neq 0$ ,  $D_{e,s} = 0$ ). The mass transport coefficient,  $k_L$ , was also included and computed as described above. The value  $D_{e,p}$  is needed to solve numerically the PVDM model. The value of  $D_{e,p}$  is needed to solve numerically the PVDM model. The optimal  $D_{e,p}$  was appraised by matching the PVDM numerical solution to the experimental concentration decay curve, along with minimizing the subsequent relationship:

$$\text{Objective relationship} = \frac{1}{N} \sum_{i=1}^N [(C_A/C_{A0})_{i,\text{exp}} - (C_A/C_{A0})_{i,\text{pred}}]^2 \quad (6.18)$$

The optimal  $D_{e,p}$  and the average percentage deviations for the PVDM are given in Table 6.3. Figure 6.4 depicts the experimental concentration decay curves for TMP (Exp. No. 3), TC (Exp. No. 8) and CPA (Exp. No. 14) adsorbing on Bent, and those predicted with PVDM model. The optimal  $D_{e,p}$  were  $14.59 \times 10^{-6}$ ,  $0.69 \times 10^{-6}$  and  $0.089 \times 10^{-6}$  cm<sup>2</sup>/s for the concentration decay curves of TMP, TC and CPA, Exp. Nos. 3, 8 and 14, respectively. Table 6.3 lists the %Dd for all the runs and were less than 5 %, expect for Exp. Nos. 1 and 11. Hence, the interpretation of the experimental data for all the runs was achieved reasonably well by the PVDM. The tortuosity factor of Bent,  $\tau_p$ , was estimated with the optimum value of  $D_{e,p}$  and the subsequent equation:

$$\tau_p = \frac{\epsilon_p D_{AB}^0}{D_{e,p}} \quad (6.19)$$

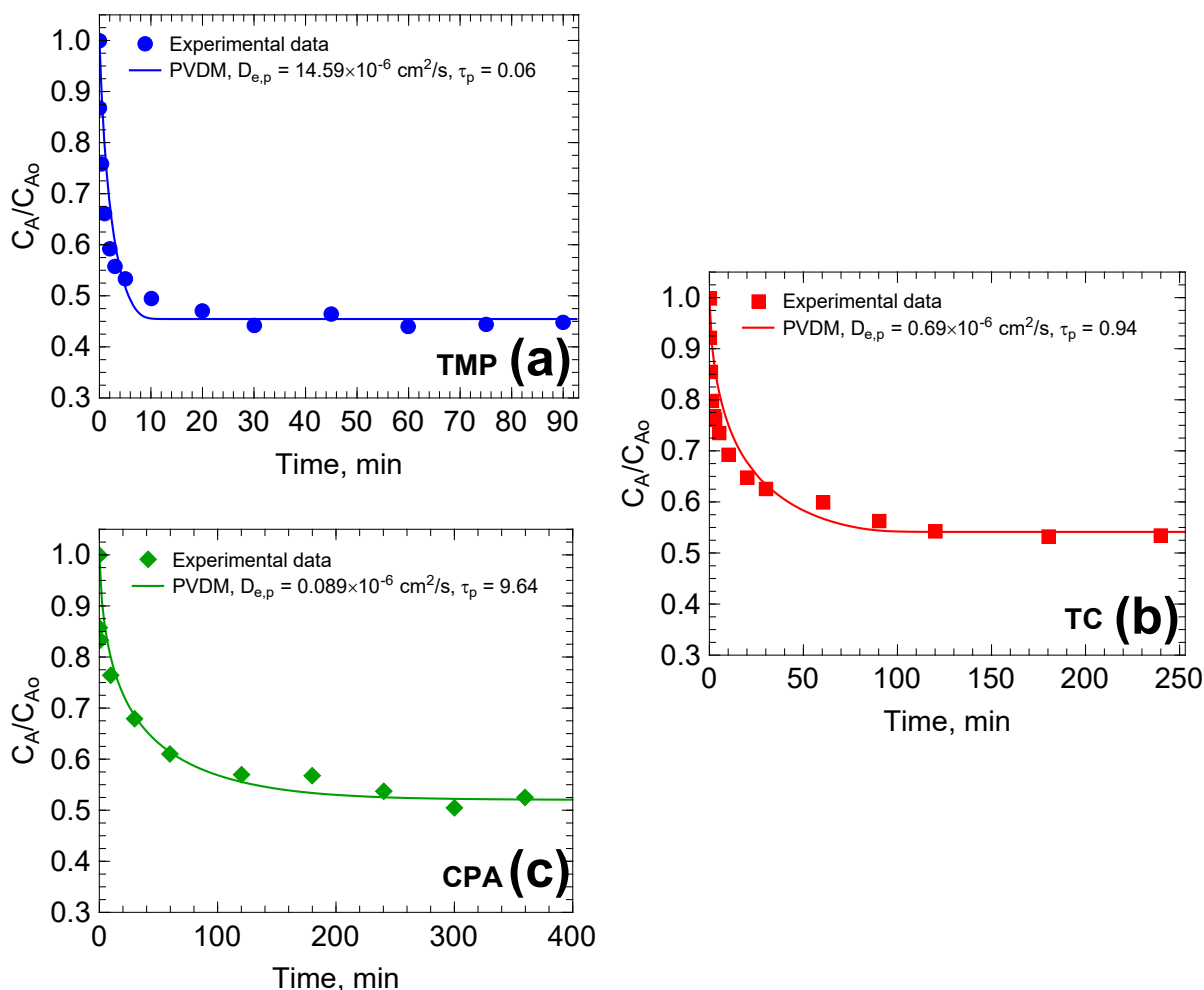
where  $D_{AB}^0$  is the molecular diffusion coefficient in dilute solution, cm<sup>2</sup>/s.

The values of  $D_{AB}^0$  for TMP, TC and CPA were estimated by the correlation suggested by Wilke and Chang (1955) in dilute water solutions and are reported in Table 6.1. Table 6.3 shows the estimated values of  $\tau_p$ , which varied from 0.03 to 0.11 for TMP, from 0.52 to 1.63 for TC, and from 9.26 and 10.07 for CPA.

The calculated values of  $\tau_p$  for the concentration decay curves of TMP (Exp. No. 3), TC (Exp. No. 8) and CPA (Exp. No. 14) were 0.06, 0.94 and 9.64, respectively. The values of  $\tau_p$  for TMP and TC are wrong and have no physical significance because  $\tau_p$  must be greater than 1. Therefore, the overall adsorption rate of TMP and TC is not exclusively due to pore volume diffusion. This result confirms that surface diffusion significantly affects intraparticle diffusion. Previous studies have cited comparable



findings. For example, the adsorption kinetics of sodium dodecylbenzenesulfonate onto different activated carbons was analyzed using the PVDM model (Leyva-Ramos et al., 2020), and  $\tau_p$  ranged from 0.63 to 1.04. However, these values did not have any physical meaning. Hence, Leyva-Ramos et al. (2020) concluded that surface diffusion also contributed to intraparticle diffusion.



**Figure 6.4.** Concentration decay curves of TMP (a), TC (b), and CPA (c) during adsorption on Bent at  $C_{A0} = 0.5 \text{ mmol/L}$  and  $T = 25^\circ\text{C}$ , for Exp. Nos. 3, 8 and 14, respectively. The lines represent the prediction of the PVDM model.

In contrast to the above, the calculated values of  $\tau_p$  for CPA were correct, confirming that intraparticle diffusion of CPA on Bent is governed mainly by pore

volume diffusion because the uptake adsorbed of CPA was less than that of TMP and TC. The values of  $\tau_p$  for Exp. Nos. 11-15 were consistently close, ranging from 9.26 to 10.07. The arithmetic average was 9.64 and can be considered as the experimental tortuosity factor of Bent ( $\tau_{p,exp}$ ).

Appelo and Wersin (2007) studied the diffusion of anions, cations and tritium oxide in opalinus clay and found that  $\tau_p$  ranged from 1.3 to 8.1; however, the  $\tau_p$  of organic molecules in natural clays has not been determined experimentally. The  $\tau_p$  value depends upon the porous structure and nature of the diffusing solute.

Several empirical tortuosity–porosity relationships have been developed to estimate the  $\tau_p$  of porous solids (Shen and Chen, 2007). The  $\tau_p$  of the Bent can be estimated from the subsequent correlation:

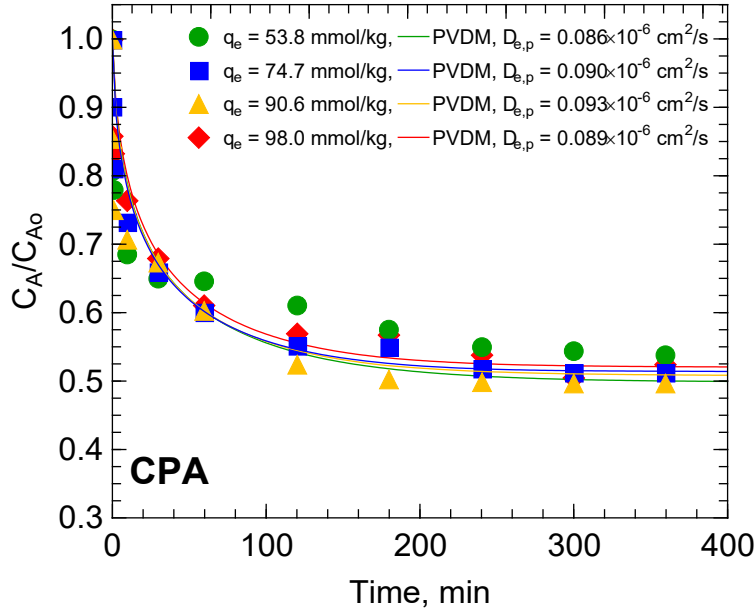
$$\tau_p = [1 - \delta(1 - \varepsilon_p)]^{-1} \quad (6.20)$$

This correlation was proposed by Pisani (2011) to estimate the tortuosity of porous materials composed of spheres, cylinders and parallelepipeds. The correlation depends on two parameters,  $\varepsilon_p$  and  $\delta$ , and the parameter  $\delta$  describes the shape of the components forming the porous structure. For Bent, the value of  $\delta$  was selected as 1.07, based on the assumption that its structure consists of parallelepipeds representing a 2:1 trilaminar structure. The calculated value of  $\tau_p$  was 8.93, close to the  $\tau_{p,exp}$  of 9.64. Hence, it can be inferred that 9.64 is a reasonable value for the  $\tau_p$  of Bent clay.

#### **6.4.5 Dependence of $D_{e,p}$ on the uptake of CPA adsorbed at equilibrium**

The influence of adsorbed uptake of CPA at equilibrium,  $q_e$ , on  $D_{e,p}$  was studied by maintaining all other operating conditions constant while varying the initial concentration of CPA. According to Figure 6.5 and Table 6.3, the PVDM model adequately fitted the experimental concentration decay data for adsorbing CPA (Exp. Nos. 11-15) independently of the  $q_e$  value. The calculated  $D_{e,p}$  were very similar for all runs and ranged slightly from  $0.086 \times 10^{-6}$  to  $0.093 \times 10^{-6}$  cm<sup>2</sup>/s (see Table 6.3). Besides,  $D_{e,p}$  did not change significantly by increasing  $q_e$ , indicating that no restricted or

hindered diffusional effects occurred in the diffusion of CPA within the pores of the Bent particle.



**Figure 6.5.** Concentration decay curves of CPA during adsorption on Bent at  $T = 25$  °C, for Exp. Nos. 11-15. The lines represent the prediction of the PVDM model.

#### 6.4.6 PVSDM model interpretation of the experimental concentration decay curves

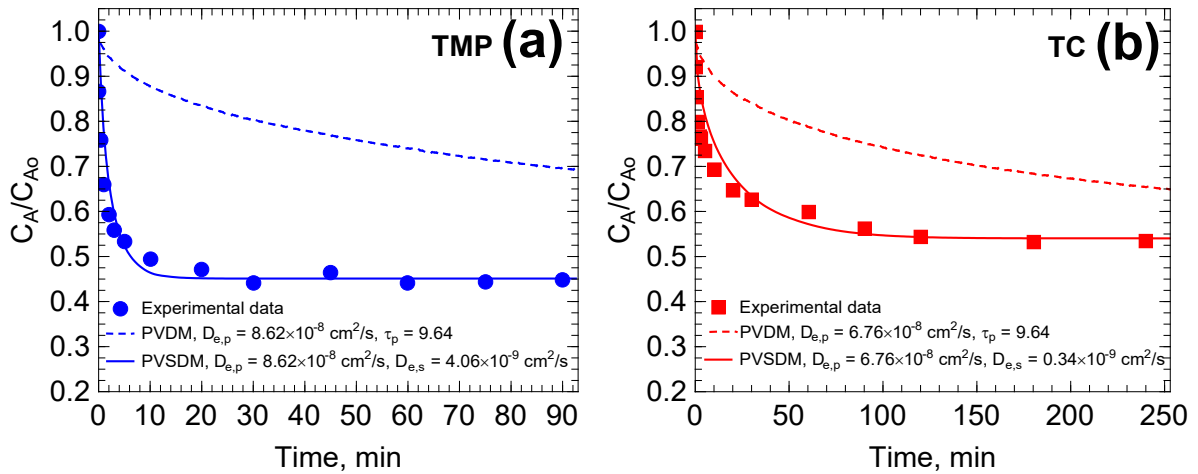
The PVSDM model supposes that surface diffusion and pore volume diffusion influence the overall adsorption rate ( $D_{e,p} \neq 0$ ,  $D_{e,s} \neq 0$ ), and the PVSDM was numerically solved for interpreting the experimental concentration decay curves of TMP and TC. The PVSDM model requires the mass transfer coefficient,  $k_L$ , as well as the intraparticle diffusion coefficients  $D_{e,p}$  and  $D_{e,s}$ . The coefficient  $D_{e,p}$  was calculated employing Equation (6.19), assuming that the  $\tau_{p,exp}$  of Bent is 9.64. The estimated  $D_{e,p}$  values for TMP and TC were  $8.62 \times 10^{-8}$  and  $6.76 \times 10^{-8}$  cm<sup>2</sup>/s, correspondingly.

The numerical solution of the PVSDM model was nonlinearly fitted to the experimental concentration decay data, and the optimal value of  $D_{e,s}$  was estimated by minimizing the objective function described in Equation (6.18). The optimal  $D_{e,s}$  for TMP and TC calculated by the PVSDM model are recorded in Table 6.3. The PVSDM model

adequately interpreted the experimental concentration decay curves for TMP and TC adsorption on Bent since the %Dd were less than 3.9 %, except for Exp. No. 1.

As illustrated in Figure 6.6, the PVSDM model reasonably predicted the experimental concentration decay curves for TMP (Exp. No. 3) and TC (Exp. No. 8) during adsorption on Bent. The optimum values of  $D_{e,s}$  were  $4.06 \times 10^{-9}$  and  $0.34 \times 10^{-9}$   $\text{cm}^2/\text{s}$  for TMP (Exp. No. 3) and TC (Exp. No. 8), respectively.

In Figure 6.6, the experimental concentration decay curves of TMP and TC are compared to those predicted by the PVDM model with  $\tau_{p,\text{exp}} = 9.64$  for TMP and TC. As seen in this figure, the PVDM model overestimated the experimental concentration decay curves of TMP and TC because the PVDM predicted a slower adsorption rate than the experimental one. Consequently, surface diffusion contributes significantly to the overall adsorption rate of TMP and TC. Similar findings were previously reported for the adsorption kinetics of ronidazole and sulfamethoxazole on granular activated carbons (Moral-Rodríguez et al., 2016).



**Figure 6.6.** Concentration decay curves of TMP (a) and TC (b) during adsorption on Bent at  $C_{A0} = 0.5 \text{ mmol/L}$  and  $T = 25 \text{ }^\circ\text{C}$ , for Exp. Nos. 3 and 8, respectively. The lines represent the prediction of the PVDM and PVSDM models.

The values of  $D_{e,s}$  for TMP and TC ranged from  $0.89 \times 10^{-9}$  to  $4.06 \times 10^{-9} \text{ cm}^2/\text{s}$  and  $0.14 \times 10^{-9}$  to  $0.46 \times 10^{-9} \text{ cm}^2/\text{s}$ , respectively. It was observed that the values of  $D_{e,s}$  of TMP were up to 7 times larger than those of  $D_{e,s}$  of TC. According to these results

(Table 6.3), surface diffusion contributes more significantly to the intraparticle diffusion of TMP compared to that of TC.

The above ranges of  $D_{e,s}$  are within the values reported in previous studies about surface diffusion in various adsorbents. The surface diffusion of ronidazole and sulfamethoxazole on granular activated carbon was analyzed in another work (Moral-Rodríguez et al., 2016), and the values of  $D_{e,s}$  for ronidazole and sulfamethoxazole were  $19.3 \times 10^{-9}$  and  $1.17 \times 10^{-9}$  cm<sup>2</sup>/s correspondingly.

#### 6.4.7 Contribution of surface diffusion to intraparticle diffusion

Surface diffusion and pore volume diffusion take place simultaneously in the intraparticle diffusion of TMP and TC during adsorption of Bent, and the contribution of each mechanism can be assessed by estimating the mass transfer fluxes driven by pore volume diffusion,  $N_{A,p}$ , and surface diffusion,  $N_{A,s}$ , expressed as follows:

$$N_{A,p} = -D_{e,p} \frac{\partial C_{Ar}}{\partial r} \quad (6.21)$$

$$N_{A,s} = -D_{e,s} \rho_p \frac{\partial q}{\partial r} \quad (6.22)$$

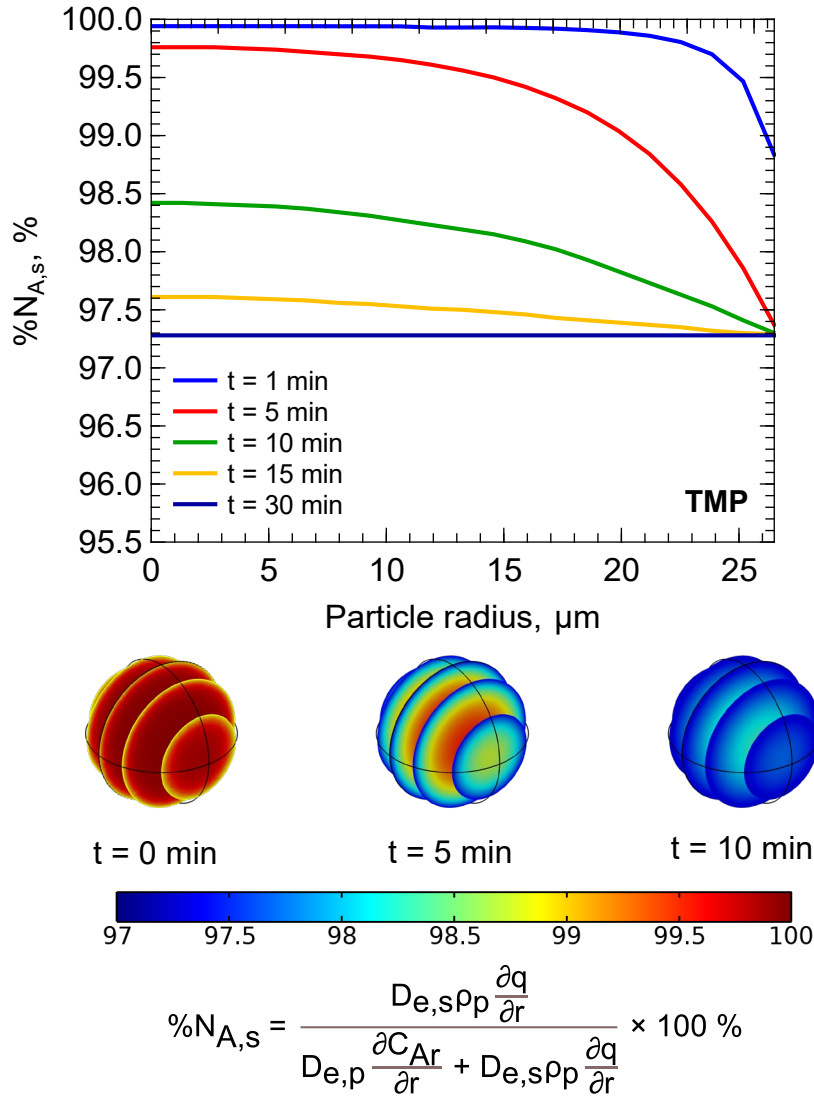
The ensuing relationship was applied to compute the percentage contribution of surface diffusion, % $N_{A,s}$ , to intraparticle diffusion:

$$\%N_{A,s} = \frac{N_{A,s}}{N_{A,p} + N_{A,s}} \times 100 \% = \frac{D_{e,s} \rho_p \frac{\partial q}{\partial r}}{D_{e,p} \frac{\partial C_{Ar}}{\partial r} + D_{e,s} \rho_p \frac{\partial q}{\partial r}} \times 100 \% \quad (6.23)$$

Figure 6.7 depicts the % $N_{A,s}$  concerning time and radius in Bent particle for the TMP adsorption rate on Bent (Exp. No. 3), and it can be seen that % $N_{A,s}$  is dependent upon time and particle radius. For example, at  $t = 5$  min, the % $N_{A,s}$  is higher than 97.4 % of the total intraparticle diffusion. Also, it can be noted that regardless of time and particle radius, % $N_{A,s}$  accounts for more than 97.3 % of the total intraparticle diffusion, whereas % $N_{A,p}$  is less than 2.7 %. This result reveals that surface diffusion predominantly controls the adsorption rate of TMP on Bent.

Comparable findings were also noted for the adsorption rate of TC on Bent, and it was estimated that the % $N_{A,s}$  accounted for more than 70 % of the total intraparticle

diffusion. Therefore, surface diffusion controls the intraparticle diffusion of TC within the Bent pores.



**Figure 6.7.** Percentage contribution of surface diffusion to the overall intraparticle diffusion as a function of time and particle radius during adsorption of TMP on Bent corresponding to Exp. No. 3.

As described in Equation (6.22), the gradient responsible for surface diffusion is the uptake adsorbed,  $q$ , and the  $\%N_{A,s}$  of TMP was higher than the  $\%N_{A,s}$  of TC because the uptake adsorbed of TMP is higher than that of TC. In contrast, the uptake adsorbed

of CPA on the Bent surface is small, so the contribution of surface diffusion of CPA to the intraparticle diffusion of CPA is negligible.

#### 6.4.8 Dependence of $D_{e,s}$ on the uptake of TMP and TC adsorbed at equilibrium

The influence of the equilibrium uptake adsorbed of TMP or TC,  $q_e$ , on  $D_{e,s}$  was analyzed by conducting experiments at different  $q_e$ . The experimental concentration decay curves for TMP and TC and the PVSDM predictions are plotted in Figures 6.8 (a) and 6.8 (b), and the results show that the PVSDM successfully modeled the experimental data for all runs of TMP and TC. According to the findings, the adsorption of TMP reaches equilibrium within 20 to 45 minutes. On the other hand, the adsorption equilibrium for TC is attained between 120 and 240 minutes. These results confirm that TMP adsorption rate is faster than TC.

As illustrated in Figures 6.8 (a) and 6.8 (b), it can be observed that  $D_{e,s}$  increases with the value of  $q_e$  for both pharmaceutical compounds. In several studies, it has been demonstrated that the increase of  $D_{e,s}$  with  $q_e$  is caused by the energy extent between the adsorbed molecule and the adsorbing sites in the solid and can be explained as follows. Initially, the solute molecules adsorb on the adsorption sites of higher energy, which results in the adsorbed molecules having insufficient energy to desorb and diffuse from one site to another. After occupying the higher energy-demanding sites, the molecules could be adsorbed on the lower energy sites, where they could desorb and diffuse more quickly. Hence,  $D_{e,s}$  would be higher by increasing  $q_e$  (Sudo et al., 1978).

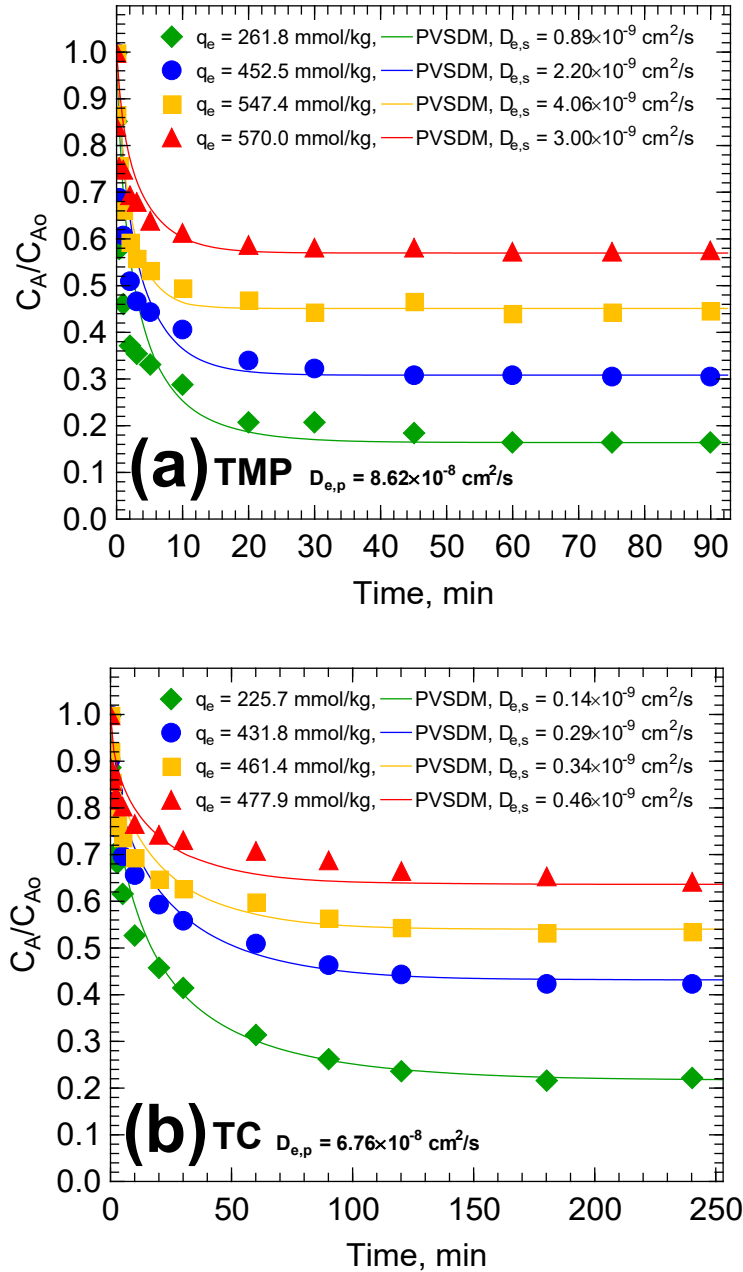
The dependence of  $D_{e,s}$  with  $q_e$  can be interpreted by the following mathematical relationship:

$$D_{e,s} = D_{sq} e^{\alpha q_e} \quad (6.24)$$

where  $D_{sq}$  is the frequency factor of the surface diffusion coefficient at  $q_e = 0$ ,  $\text{cm}^2/\text{s}$ ;  $\alpha$  is a fitting constant,  $\text{kg}/\text{mmol}$ .

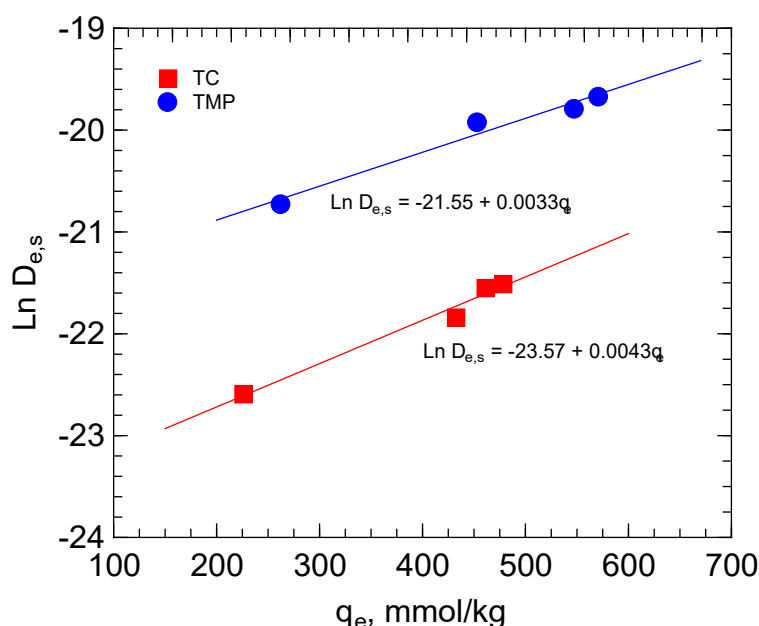
This equation has been applied in previous works about surface diffusion (Ocampo-Perez et al., 2011a). A nonlinear least-squares approach was performed to fit Equation (6.24) to the experimental values of  $D_{e,s}$  vs.  $q_e$ . The optimal values of  $D_{sq}$

and  $\alpha$  were  $4.37 \times 10^{-10} \text{ cm}^2/\text{s}$  and  $0.0033 \text{ kg}/\text{mmol}$  for TMP and  $0.58 \times 10^{-10} \text{ cm}^2/\text{s}$  and  $0.0043 \text{ kg}/\text{mmol}$  for TC. Figure 6.9 depicts the influence of  $q_e$  upon  $D_{e,s}$ , and it can be noted that Equation (6.24) interpreted the experimental data satisfactorily.



**Figure 6.8.** Concentration decay curves of TMP (a) and TC (b) during adsorption on Bent at  $T = 25 \text{ }^\circ\text{C}$ , for Exp. Nos. 1-4 and 6-9, respectively. The lines represent the prediction of the PVSDM model.





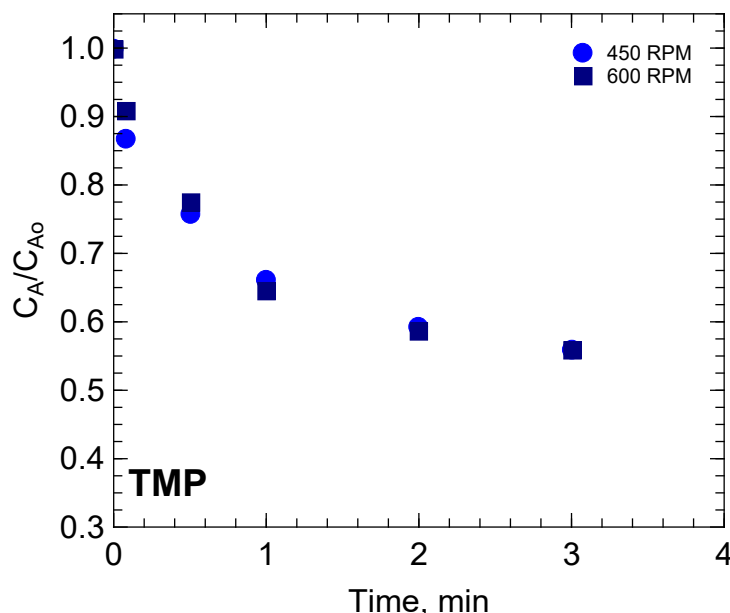
**Figure 6.9.** Effect of the uptake of TMP and TC adsorbed at equilibrium on  $D_{e,s}$ .

#### 6.4.9 Importance of external mass transport to the adsorption rate of TMP, TC and CPA

Previous studies (Ocampo-Perez et al., 2011a) investigated the adsorption rate of organic compounds on organobentonite, and the concentration decay data were procured in a stirred tank batch adsorber similar to the one used in this work. The findings showed that agitation speed over the 300 – 500 RMP range did not affect the concentration decay curves. The influence of external mass transport on the adsorption rate of TMP, TC and CPA was investigated by conducting experiments under constant operating conditions at the stirring speeds of 450 and 600 RPM. The stirring speed was varied because it played a crucial role in the external mass transfer.

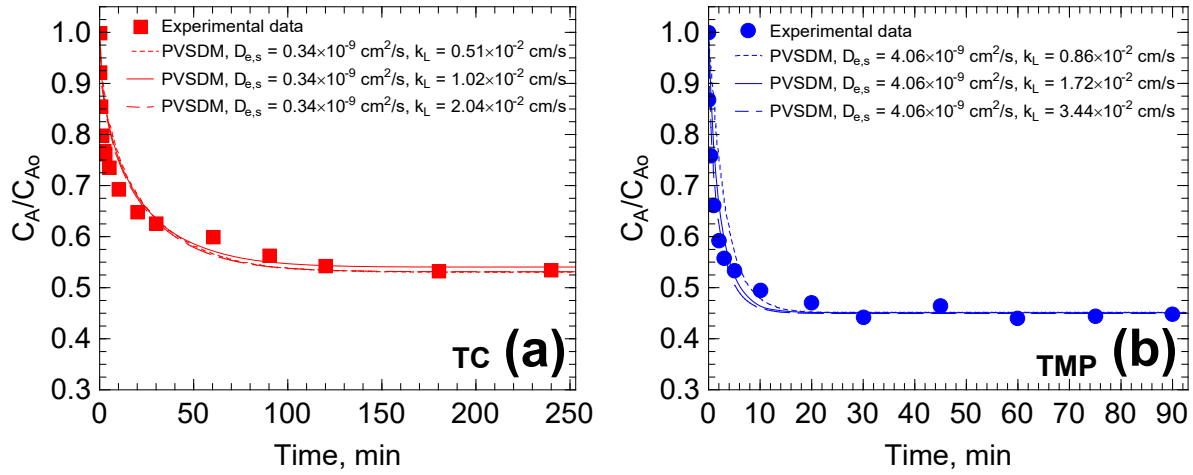
The experimental concentration decay curves for TMP adsorption on Bent at the stirring speeds of 450 RPM (Exp. No. 3) and 600 RPM (Exp. No. 5) at times less than 4 min are shown in Figure 6.10. The experimental concentration decay curve at 450 RPM overlaps that at 600 RPM, corroborating that the external mass transfer is not affecting the overall adsorption rate of TMP. Besides, the results in Table 6.3 show that the estimated values of  $D_{e,s}$  for 450 and 600 RPM are the same and equal to  $4.06 \times 10^{-6}$

$^9 \text{ cm}^2/\text{s}$ . Comparable results were found for the concentration decay curves of TC (Exp. Nos. 8 and 10) and CPA (Exp. Nos. 14 and 15). Therefore, the adsorption rate does not depend on the external mass transfer for the stirring speeds of 450 RPM or higher.



**Figure 6.10.** Effect of stirring rate on the concentration decay curves of TMP during adsorption on Bent at  $T = 25 \text{ }^\circ\text{C}$ , for Exp. Nos. 3 and 5. The lines represent the prediction of the PVSDM model.

The effect of the external mass transfer on the adsorption rate of TMP and TC was further investigated by comparing the PVSDM prediction of the concentration decay varying the mass transfer coefficient. The concentration decay of TMP and TC predicted with PVSDM and the best value of  $D_{e,s}$  and three values of  $k_L$  are displayed in Figure 6.11. The  $k_L$  values used were the  $k_L$  estimated by the method described in the Section 6.4.3, and this  $k_L$  was doubled and halved. The results demonstrate that the concentration decay predicted with PVSDM do not essentially change varying  $k_L$ , corroborating that the mass transfer does not affect the adsorption rate of TMP and TC on Bent.



**Figure 6.11.** Effect of  $k_L$  on the concentration decay curves of TC (a) and TMP (b) during adsorption on Bent at  $T = 25^\circ\text{C}$ , for Exp. Nos. 8 and 3, respectively. The lines represent the prediction of the PVSDM model.

## 6.5 Conclusions

In this work, the adsorption rate of TMP, TC and CPA on Bent was interpreted using the EMTM and PVSDM diffusion models. The adsorption occurred in the intraparticle and interlayer spaces of Bent and is governed by both physical and chemical mechanisms such as electrostatic attractions and cation exchange.

The EMTM model did not interpret the experimental data of the decay curves, demonstrating that the external mass transfer does not affect the adsorption rate and the intraparticle diffusion is essential.

Interpretation by the PVSDM model showed a good fit of the kinetic data. The overall adsorption rate of TMP and TC is due to surface diffusion and pore volume diffusion, and the values of  $D_{e,s}$  increased with the values of  $q_e$ . Conversely, pore volume diffusion controls the overall adsorption rate of CPA and no variation of  $D_{e,p}$  was recorded with increasing the value of  $q_e$ , allowing to estimate an experimental tortuosity factor of 9.64. It was revealed that the intraparticle diffusion mechanisms depend on the adsorption capacity. At higher adsorption capacities, there is an increase in the gradients of uptake adsorbed that rises surface diffusion. Contrarily, the uptake adsorbed of CPA is so small that surface diffusion of CPA is negligible.

# CHAPTER

# 7

**COMPETITIVE AND  
COOPERATIVE BINARY  
ADSORPTION OF  
TETRACYCLINE AND  
CADMIUM (II) ONTO 2:1  
LAYERED CALCIUM BENTONITE  
CLAY FROM AQUEOUS  
SOLUTIONS**

## **7.1 Introduction**

The presence of antibiotics in water sources has emerged as a significant environmental concern due to their potential adverse effects on ecosystems (Kovalakova et al., 2020). This concern stems by their strong persistence in the environment and the development of highly resistant bacteria, which can have profound implications for both environmental and human health (Kulik et al., 2023).

Tetracycline (TC), a broad-spectrum antibiotic widely used to treat a variety of microbial infections such as anthrax, chlamydial infections, cholera, Lyme disease, and syphilis, is also extensively employed in veterinary medicine for the treatment of farm animals and domestic pets (Chopra and Roberts, 2001). Due to its high consumption, TC has been detected at elevated levels in water bodies (Leichtweis et al., 2022). According to Xu et al. (2021), TC has been found in concentrations ranging from 1.1 to 54,000 ng/L in rivers, 17.8 to 745 ng/L in lakes, 1.55 to 2,500 ng/L in seawater, 9.51 to 29,700 ng/L in groundwater, 11.2 to 632 ng/L in drinking water, and 0.001 to 12,000 µg/L in wastewater systems, significantly impacting the life of aquatic organisms and posing risks to human health. Therefore, the removal of this antibiotic from water is crucial.

In recent research, a variety of materials have been developed to target the removal of TC through adsorption processes. Noteworthy among these are Fe-based metal-organic frameworks, which achieved an impressive adsorption capacity of 340 mg/g (Zhang et al., 2021). Additionally, sheet-like graphitized carbon demonstrated an adsorption capacity of 138.32 mg/g (Ao et al., 2024), while graphene oxide exhibited promising results with an adsorption capacity of 133 mg/g (Li et al., 2023). Magnetic mesoporous silica and KMnO<sub>4</sub>-modified biochar have also been investigated, showing adsorption capacities of 20 mg/g (Hanh et al., 2023) and 107.77 mg/g (Huang et al., 2023), respectively.

In a previous work, Ortiz-Ramos et al. (2022) identified bentonite clay as a promising adsorbent for TC, with a maximum adsorption capacity of 283.5 mg/g. This remarkable capacity competes with that of other adsorbents, highlighting the efficacy of bentonite clay in TC removal. Moreover, the use of bentonite clay offers distinct

advantages such as its low cost and abundance compared to alternative materials, making it an attractive option for water treatment applications.

Bentonite is a type of clay belonging to the smectite group, characterized by a 2:1 layered structure predominantly composed of montmorillonite. Its structure consists of an octahedral sheet containing  $\text{Al}^{3+}$  ions sandwiched between two tetrahedral sheets containing  $\text{Si}^{4+}$  ions. Isomorphous substitutions of cations within these sheets generate an excess of negative charge, which is balanced by exchangeable and hydratable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  present in the interlayer space. These cations form weak bonds, contributing to the high cation exchange capacity and swelling properties of the clay. As a result, bentonite exhibits the ability to adsorb heavy metals on its surface through cation exchange mechanisms (Chang et al., 2020; Dhar et al., 2023; Hussain and Ali, 2021; Padilla-Ortega et al., 2020).

Multiple studies have highlighted the impact of combined heavy metal pollution, including  $\text{Cd(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Zn(II)}$  and  $\text{Ni(II)}$ , on the adsorption behavior of certain contaminants. For instance, Wang and You (2023) investigated the adsorption of norfloxacin, sulfadiazine,  $\text{Ni(II)}$  and  $\text{Cu(II)}$  on a functionalized-chitosan magnetic composite in both single and binary systems. Their findings revealed that the presence of  $\text{Cu(II)}$  and norfloxacin together promoted the sorption of each other, while no significant synergy was observed between  $\text{Ni(II)}$  and sulfadiazine. Similarly, researchers explored the simultaneous adsorption of  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ , tetracycline and sulfadiazine on graphene oxides, demonstrating that heavy metals enhanced the adsorption capacities for antibiotics, whereas antibiotics only slightly promoted the adsorption capacities for heavy metals (Yao et al., 2020). Additionally, research by Yang et al. (2020) investigated the simultaneous adsorption of tetracycline and  $\text{Cd(II)}$  onto dodecyl dimethyl betaine-modified vermiculite, observing a slight enhancement in the adsorption capacities of both TC and  $\text{Cd(II)}$  in the presence of each other.

In the literature, research on the adsorption of pharmaceutical compounds using raw clays remains relatively underexplored. Furthermore, the simultaneous adsorption of antibiotics and heavy metals on bentonite clay has yet to be thoroughly investigated. In this regard, Chapter 7 aims to investigate the binary adsorption of TC and  $\text{Cd(II)}$

under varying solution pH conditions using raw bentonite clay. Samples of bentonite saturated with TC and Cd(II) in both single and binary solutions were prepared and characterized using XRD and XPS analysis. Binary adsorption isotherms were adequately constructed and interpreted using modified and extended multicomponent models derived from single adsorption isotherms. Additionally, displacement experiments of TC by Cd(II) and vice versa were conducted. Finally, the binary adsorption mechanisms as a function of solution pH were elucidated, providing valuable insights into the complex interactions between antibiotics and heavy metals in aquatic environments.

## **7.2 Experimental methodology**

### **7.2.1 Materials and characterization**

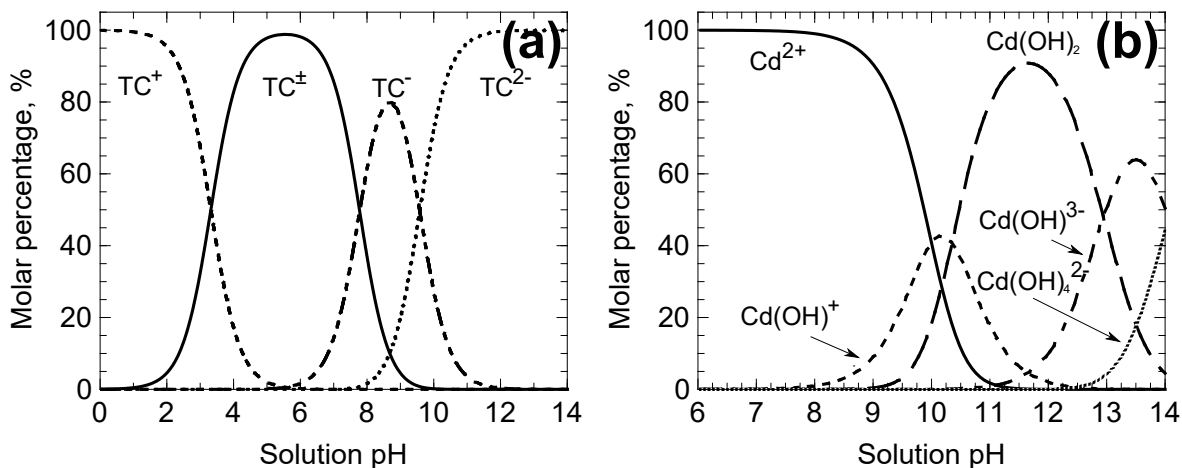
Calcium bentonite (Bent) was sourced from a mineral deposit situated in San Luis Potosi, Mexico. The extraction and conditioning technique of Bent are detailed in Chapter 4.

TC as an anhydrous form (CAS: 60-54-8) was supplied by Merck, while Cd(II) in the form of  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  (CAS: 7790-78-5) was provided by Fermont. In aqueous solutions, TC donates protons and exhibits four chemical species depending on the solution's pH. The cationic species ( $\text{TC}^+$ ) predominates at a pH below 3.32, the zwitterionic species ( $\text{TC}^\pm$ ) at pH values between 3.32 and 7.78, and the anionic species ( $\text{TC}^-$  and  $\text{TC}^{2-}$ ) at pH values higher than 7.78. Cd(II) exists as a free ion ( $\text{Cd}^{2+}$ ) at pH values below 7.5, whereas at higher values, Cd(II) precipitates as cadmium hydroxide, forming the following chemical species:  $\text{CdOH}^+$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_4^{2-}$  y  $\text{Cd}(\text{OH})_3^-$ . Speciation diagrams for TC and Cd(II) at a total concentration of 0.5 mmol/L are presented in Figure 7.1.

### **7.2.2 Characterization of bentonite with TC and Cd(II) adsorbed**

The characterization of Bent involved several techniques, including  $\text{N}_2$  physisorption, SEM, XRD, TGA, FT-IR and Zeta potential. A comprehensive description of the methodology can be found in a prior study (Ortiz-Ramos et al., 2022). The

estimated textural properties from this investigation were as follows:  $S_{\text{BET}} = 44.5 \text{ m}^2/\text{g}$ ,  $V_p = 0.086 \text{ cm}^3/\text{g}$  and  $D_p = 7.72 \text{ nm}$ . The cation exchange capacity (CEC) was determined to be  $75.2 \text{ cmol}(+)/\text{kg}$ , and the isoelectric point of Bent was found to be less than 2, indicating a negatively charged surface at pH values above 2.



**Figure 7.1.** Speciation diagrams of TC (a) and Cd(II) (b) at an equilibrium concentration of 0.5 mmol/L.

Bent samples were saturated with TC and Cd(II) in both single and binary solutions at pH values of 3 and 7 and at  $T = 25^\circ\text{C}$ . The saturation procedure will be discussed in Section 7.2.4. The saturated samples were designated as Bent-Cd3, Bent-TC3 and Bent-TC/Cd3 for saturation at pH = 3, and as Bent-Cd7, Bent-TC7 and Bent-TC/Cd7 for saturation at pH = 7. Bent-Cd samples refer to Bent saturated with Cd(II) in a single solution ( $q_{\text{Cd(II)}} = 48.9 \text{ cmol}(+)/\text{kg}$  at pH = 3,  $q_{\text{Cd(II)}} = 55.1 \text{ cmol}(+)/\text{kg}$  at pH = 7), Bent-TC samples to Bent saturated with TC in a single solution ( $q_{\text{TC}} = 57.9 \text{ cmol}(+)/\text{kg}$  at pH = 3,  $q_{\text{TC}} = 34.5 \text{ cmol}(+)/\text{kg}$  at pH = 7) and Bent-TC/Cd samples to Bent saturated with both TC and Cd(II) in a binary solution ( $q_{\text{Cd(II)}+\text{TC}} = 51.0 \text{ cmol}(+)/\text{kg}$  at pH = 3,  $q_{\text{Cd(II)}+\text{TC}} = 110.9 \text{ cmol}(+)/\text{kg}$  at pH = 7). The samples were characterized by XRD using a Rigaku X-ray diffractometer, model Ultima IV, operating under conditions: Cu-K $\alpha$  ( $\lambda = 0.15406 \text{ nm}$ ), 44 mA and 40 kV. The scanning range was from  $4$  to  $21^\circ$  ( $2\theta$ ) at a rate of  $1.8^\circ/\text{min}$ , and the identified phases were determined by comparison with the standard JCPDS 13-0135. XPS analyses were carried out using a Kratos Axis Ultra-



DLD spectrometer, featuring a hemispherical electron analyzer coupled with a DLD (delay-line detector) and an Al-K $\alpha$  monochromator powered at 600 W. The x-ray source employed was a Mg/Al double anode rated at 450 W.

### **7.2.3 Quantification of TC and Cd(II) concentrations in aqueous solutions**

The quantification of TC concentrations in both single and binary solutions was carried out using a Shimadzu UV-Vis spectrophotometer, model 2600. Initially, a drop of HCl 10 M was added to each sample to reduce the solution pH to 1 and dissociate the TC-Cd(II) complexes. The spectrophotometer was configured with a wavelength of 357 nm, and the absorbances of the samples were recorded. TC concentrations were determined using calibration curves established from standard TC solutions with concentrations ranging from 0.5 to 42 mg/L, each with a drop of HCl 10 M added before analysis.

Cd(II) concentrations were measured using a Varian atomic absorption spectrophotometer, model SpectrAA-220. The absorbance of the samples was assessed at 326.1 nm. Calibration curves, spanning concentrations from 5 to 600 mg/L, were employed to determine Cd(II) concentrations in both single and binary solutions.

### **7.2.4 Method for obtaining adsorption equilibrium data**

The experimental data for the adsorption equilibrium of TC and Cd(II) on Bent in both single and binary solutions were obtained through batch adsorption experiments, as detailed below. The experiments were conducted at pH values of 3 and 7. Initially, single and binary solutions of TC and Cd(II) with varying initial concentrations were prepared. A total of 42 solutions were formulated in volumetric flasks, with concentrations ranging from 10 to 250 mg/L for TC and from 30 to 550 mg/L for Cd(II). These solutions were calibrated in a solution of constant ionic strength prepared by combining HCl 0.01 N and NaOH 0.01 N. Subsequently, 40 mL of each single or binary solution was added to a 50 mL centrifuge vial, referred to as batch adsorber, containing 0.05 g of Bent. The adsorbers were placed in a water bath at 25 °C, and the solution

pH was daily adjusted to 3 or 7 using drops of solutions of HCl 0.01 N or NaOH 0.01 N, with the added volume kept below 0.5 mL.

Adsorption equilibrium was considered achieved in 7 days, as the concentrations of TC and Cd(II) in both single and binary solutions remained constant. Upon reaching equilibrium, the samples were centrifuged at 2500 rpm for 10 min. An aliquot of each solution was filtered, and the concentrations of TC and Cd(II) in both single and binary solutions were quantified using the procedure described in Section 7.2.3. The uptake of TC and Cd(II) adsorbed in both single and binary solutions on Bent, expressed in units of cmol(+)/kg, was calculated using the mass balance described by the following equation:

$$q_i = \frac{(C_{i,o} - C_i) \times V \times 100}{m \times EW_i} \quad (7.1)$$

where  $q_i$  is the uptake of component  $i$  adsorbed on Bent, cmol(+)/kg;  $C_{i,o}$  is the initial concentration of component  $i$ , mg/L;  $C_i$  is the concentration of component  $i$  at equilibrium, mg/L;  $V$  is the solution volume, L;  $m$  is the mass of Bent, g;  $EW_i$  is the equivalent weight of component  $i$ , g/eq.

### 7.2.5 Technique for performing the displacement experiments

Displacement experiments involve the initial adsorption of contaminant  $i$  in a single solution, followed by the addition of contaminant  $j$ . The objective is to quantify the percentage of contaminant  $i$  displaced due to the adsorption of contaminant  $j$ . This procedure unfolds in two distinct steps, outlined below. Initially, the single adsorption equilibrium of TC and Cd(II) at pH values of 3 and 7 was obtained employing the methodology described in Section 7.2.4. The uptake of TC and Cd(II) adsorbed in the first adsorption equilibrium,  $q_{i,1}$  was subsequently determined. In the second step, an aliquot of a concentrated solution containing TC and Cd(II), as corresponding, was added to each adsorber. These solutions were contacted for an additional 7 days until both contaminants reached a subsequent adsorption equilibrium, referred to as the second adsorption equilibrium,  $q_{i,2}$ . Finally, the uptake adsorbed during this second

adsorption equilibrium was determined, and the percentage of TC and Cd(II) displaced was estimated using the equation:

$$\% \text{Desp} = \frac{q_{i,1} - q_{i,2}}{q_{i,1}} \times 100 \% \quad (7.2)$$

where %Desp is the percentage of component  $i$  displaced by component  $j$ , %;  $q_{i,1}$  is the uptake of component  $i$  adsorbed on Bent at first equilibrium, cmol(+)/kg;  $q_{i,2}$  is the uptake of component  $i$  adsorbed on Bent at second equilibrium, cmol(+)/kg.

## 7.3 Results and discussion

### 7.3.1 Equations of single and binary adsorption isotherms

The experimental data of the single adsorption equilibrium of TC and Cd(II) on Bent were interpreted using conventional adsorption isotherm models, including Freundlich, Langmuir and Redlich-Peterson. These models are described by the following mathematical expressions:

a) Freundlich isotherm:

$$q_i = k_i C_i^{1/n_i} \quad (7.3)$$

b) Langmuir isotherm:

$$q_i = \frac{q_{m,i} K_i C_i}{1 + K_i C_i} \quad (7.4)$$

c) Redlich-Peterson isotherm:

$$q_i = \frac{a_i C_i}{1 + b_i C_i^{\beta_i}} \quad (7.5)$$

where  $k_i$  is the Freundlich isotherm parameter of component  $i$ , cmol(+)<sup>1-1/ $n_i$</sup>  L<sup>1/ $n_i$</sup> /kg;  $n_i$  is the Freundlich isotherm parameter of component  $i$ ;  $q_{m,i}$  is the Langmuir isotherm parameter of component  $i$ , cmol(+)/kg;  $K_i$  is the Langmuir isotherm parameter of component  $i$ , L/cmol(+);  $a_i$  is the Redlich-Peterson isotherm parameter of component  $i$ , L/kg;  $b_i$  is the Redlich-Peterson isotherm parameter of component  $i$ , (L/cmol(+)) <sup>$\beta_i$</sup> ;  $\beta_i$  is the Redlich-Peterson isotherm parameter of component  $i$ .

The best-fit parameters of the single adsorption isotherms were determined using the Rosenbrock-Newton algorithm. The average deviation percentages for each isotherm were then calculated using the following equation:

$$\%D = \frac{1}{N} \sum_{i=1}^N \left| \frac{q_{i,\text{exp}} - q_{i,\text{pred}}}{q_{i,\text{exp}}} \right| \times 100\% \quad (7.6)$$

where %D is the average percentage deviation, %;  $q_{i,\text{exp}}$  is the experimental uptake of component  $i$  adsorbed on Bent in single solution, cmol(+)/kg;  $q_{i,\text{pred}}$  is the uptake predicted of component  $i$  adsorbed on Bent in single solution, cmol(+)/kg;  $N$  is the number of components in solution.

Table 7.1 shows the estimated parameters of the single adsorption isotherms along with the corresponding average deviation percentages. The Langmuir isotherm was selected as the most suitable model for predicting the experimental data of the single adsorption equilibrium of TC and Cd(II). This choice is justified by the Langmuir isotherm exhibiting average deviation percentages less than 7 %, which were lower than those estimated by the Freundlich and Redlich-Peterson isotherms.

**Table 7.1.** Single adsorption isotherm parameters and average deviation percentages for the adsorption of TC and Cd(II) on Bent.

| Solutes | pH | Freundlich                                           |      |      | Langmuir                       |                  |     | Redlich-Peterson |                               |      |     |
|---------|----|------------------------------------------------------|------|------|--------------------------------|------------------|-----|------------------|-------------------------------|------|-----|
|         |    | K<br>(cmol(+) <sup>1-1/n</sup> L <sup>1/n</sup> /kg) | n    | %D   | q <sub>m</sub><br>(cmol(+)/kg) | K<br>(L/cmol(+)) | %D  | a<br>(L/kg)      | b<br>(L/cmol(+)) <sup>β</sup> | β    | %D  |
| TC      | 3  | 413.2                                                | 2.14 | 16.0 | 82.7                           | 165.10           | 4.2 | 13003.8          | 153.4                         | 1.00 | 5.0 |
|         | 7  | 262.0                                                | 2.14 | 14.5 | 54.8                           | 149.40           | 4.2 | 7026.6           | 118.4                         | 1.00 | 4.2 |
| Cd(II)  | 3  | 87.7                                                 | 1.56 | 10.5 | 84.4                           | 3.27             | 1.6 | 297.4            | 3.33                          | 0.89 | 1.7 |
|         | 7  | 90.4                                                 | 1.95 | 13.2 | 73.8                           | 6.93             | 6.1 | 653.9            | 8.09                          | 0.83 | 6.9 |

The binary adsorption equilibrium of TC and Cd(II) on Bent was modeled by fitting the experimental data with modified and extended models derived from single adsorption isotherms. In this study, the following multicomponent models were employed:

a) Sheindorf-Rebuhn-Sheintuch isotherm (SRS):

$$q_i = k_i C_i \left( \sum_{j=1}^N a_{ij} C_j \right)^{\left( \frac{1}{\eta_i} \right) - 1} \quad (7.7)$$

where  $a_{ii} = a_{jj} = 1$ .

b) Extended Freundlich Multicomponent isotherm (EFM):

$$q_1 = \frac{k_1 C_1^{\left( \frac{1}{\eta_1} \right) + x_1}}{C_1^{x_1} + y_1 C_2^{z_1}} \quad q_2 = \frac{k_2 C_2^{\left( \frac{1}{\eta_2} \right) + x_2}}{C_2^{x_2} + y_2 C_1^{z_2}} \quad (7.8)$$

c) Modified Langmuir Multicomponent isotherm (MLM):

$$q_i = \frac{q_{m,i} K_i \left( C_i / \eta_i \right)}{1 + \sum_{j=1}^N K_j \left( C_j / \eta_j \right)} \quad (7.9)$$

d) Extended Langmuir Multicomponent isotherm (ELM):

$$q_i = \frac{q_{\max} K_{e,i} C_i}{1 + \sum_{j=1}^N K_{e,j} C_j} \quad (7.10)$$

e) Modified Redlich-Peterson Multicomponent isotherm (MRPM):

$$q_i = \frac{a_i \left( C_i / \eta_i \right)}{1 + \sum_{j=1}^N b_j \left( C_j / \eta_j \right)^{\beta_j}} \quad (7.11)$$

where  $a_{ij}$  is the competition coefficient of component  $i$  by component  $j$ ;  $x_i$ ,  $y_i$  and  $z_i$  are the Extended Freundlich Multicomponent isotherm parameters of component  $i$ ;  $\eta_i$  is the interaction factor of component  $i$ ;  $q_{\max}$  is the Extended Langmuir Multicomponent isotherm parameter, cmol(+)/kg;  $K_{e,i}$  is the Extended Langmuir Multicomponent isotherm parameter of component  $i$ , L/cmol(+).

The interaction parameters of multicomponent adsorption isotherms were estimated using the following equations, employing the Levenberg-Marquardt algorithm:

$$\text{Objective relationship} = \sum_{i=1}^2 \sum_{j=1}^{N_m} \left( q_{ij,\text{exp}} - q_{ij,\text{pred}} \right)^2 \quad (7.12)$$

$$\%D = \left[ \frac{1}{2} \sum_{i=1}^2 \frac{1}{N_m} \sum_{j=1}^{N_m} \left| \frac{q_{ij,\text{exp}} - q_{ij,\text{pred}}}{q_{ij,\text{exp}}} \right| \right] \times 100 \% \quad (7.13)$$

where  $N_m$  is the number of experimental data;  $q_{ij,\text{exp}}$  is the experimental uptake of component  $i$  adsorbed on Bent corresponding to data  $j$  in binary solution,  $\text{cmol}(+)/\text{kg}$ ;  $q_{ij,\text{pred}}$  is the uptake predicted of component  $i$  adsorbed on Bent corresponding to data  $j$  in binary solution,  $\text{cmol}(+)/\text{kg}$ .

Table 7.2 details the computed interaction parameters and average deviation percentages for binary adsorption isotherms of TC and Cd(II) on Bent at  $\text{pH} = 3$ . It is noteworthy that the experimental data of binary adsorption of TC and Cd(II) on Bent at  $\text{pH} = 7$  could not be successfully fitted by any of the binary adsorption isotherm models. The interpretation of this data will be discussed upon in subsequent discussions.

The selection of the best-fit adsorption isotherm model involved careful consideration of average deviation percentages, parameter values, and the physical interpretation of interaction factors. The EFM, ELM and MRPM models exhibited the lowest average deviation percentages. In Figure 7.2, a comparison is illustrated between the experimental uptakes adsorbed and those predicted by the EFM, ELM and MRPM models. The blue lines represent a 20 % deviation, both overestimate and underestimate. Notably, the majority of experimental data falls within the 20 % deviation lines.

The EFM model exhibited an average deviation percentage of 15.4 %, but involved six fit parameters that do not adequately explain the interactions between TC and Cd(II) (McKay and Al-Duri, 1991). In contrast, the ELM model considered three interaction parameters related to the Langmuir isotherm but neglects the parameters of the single adsorption isotherms of TC and Cd(II) on Bent. The MRPM model, with an average deviation percentage of 18.7 %, incorporated two parameters representing the interaction nature between two different contaminants and six parameters of the single adsorption isotherms (Mathews, 1975; Schay et. al., 1957). In this context, the MRPM model was selected to fit the experimental data of binary adsorption equilibrium of TC and Cd(II) on Bent at  $\text{pH} = 3$ .

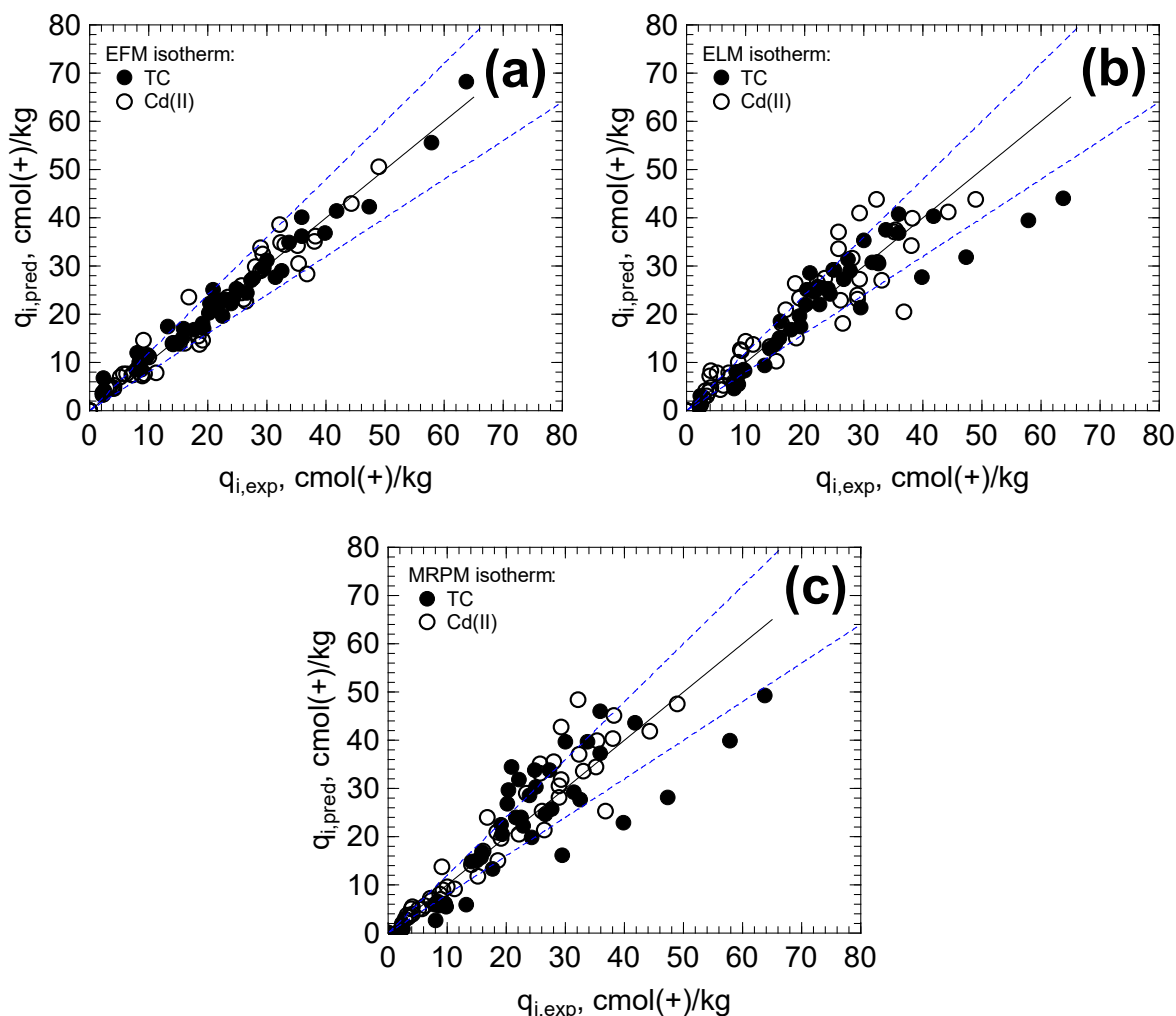
**Table 7.2.** Parameters and average deviation percentage of the multicomponent adsorption isotherm models for the binary adsorption of TC and Cd(II) on Bent at pH = 3.

| Model | Parameters of the single isotherms | Interaction factors | Parameters                                                                                                           | %D   |
|-------|------------------------------------|---------------------|----------------------------------------------------------------------------------------------------------------------|------|
| SRS   | 4                                  | 4                   | $a_{Cd,Cd} = 1.0$<br>$a_{Cd,TC} = 61.2$<br>$a_{TC,TC} = 1.0$<br>$a_{TC,Cd} = 0.38$                                   | 22.6 |
| EFM   | 4                                  | 6                   | $x_{TC} = 0.028$<br>$y_{TC} = 0.986$<br>$z_{TC} = 0.480$<br>$x_{Cd} = 0.066$<br>$y_{Cd} = 0.704$<br>$z_{Cd} = 0.103$ | 15.4 |
| MLM   | 4                                  | 2                   | $\eta_{TC} = 2.65$<br>$\eta_{Cd} = 1.14$                                                                             | 19.5 |
| ELM   | 0                                  | 3                   | $q_{max} = 56.08$<br>$K_{e,TC} = 172.5$<br>$K_{e,Cd} = 8.5$                                                          | 19.1 |
| MRPM  | 6                                  | 2                   | $\eta_{TC} = 2.36$<br>$\eta_{Cd} = 1.07$                                                                             | 18.7 |

### 7.3.2 Adsorption isotherms of TC and Cd(II) in single solution

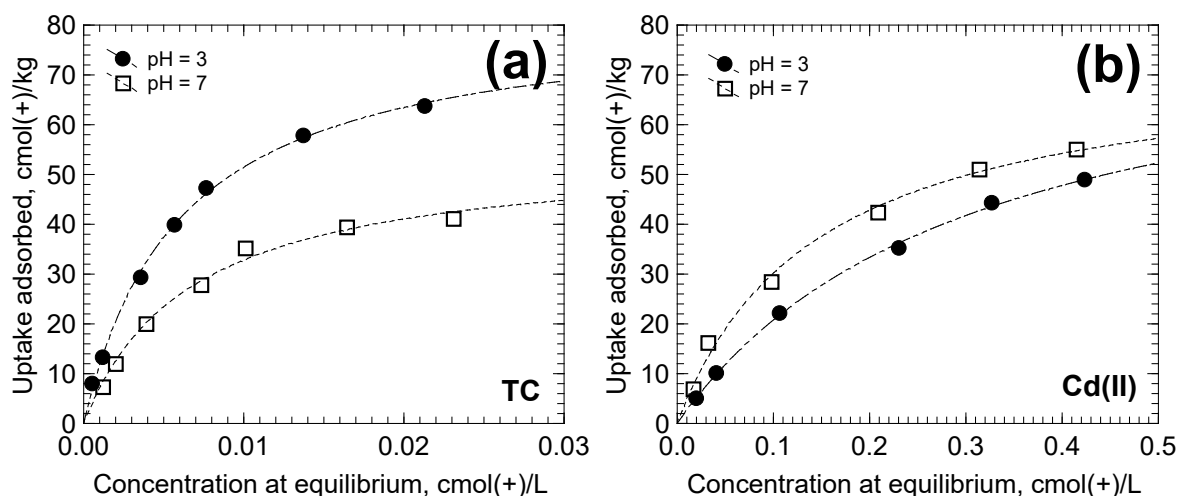
Figure 7.3 illustrates the single adsorption isotherms of TC and Cd(II) on Bent at  $T = 25\text{ }^{\circ}\text{C}$  and pH values of 3 and 7. In Figure 7.3 (a), it is evident that the maximum adsorption capacity of Bent for TC was  $63.8\text{ cmol(+)}/\text{kg}$  ( $283.5\text{ mg/g}$ ) at pH = 3 and decreased with an increase in solution pH. A prior investigation, Ortiz-Ramos et al. (2022) elucidated the adsorption mechanisms of TC on Bent, revealing that TC adsorption occurs within the interlayer space and on the external surface of Bent. This process is highly pH-dependent due to changes in the surface charge of Bent and the chemical species of TC. At pH = 3, the maximum adsorption capacity is controlled by

electrostatic attraction between  $\text{TC}^+$  and the negatively charged surface of Bent, coupled with cation exchange between  $\text{TC}^+$  and the  $\text{Ca}^{2+}$  interlayer cations. The reduction in adsorption capacity at  $\text{pH} = 7$  is attributed to weak electrostatic interaction between the positively charged dimethylamino group of  $\text{TC}^\pm$  species and the negatively charged surface of Bent, as well as the formation of coordination complexes between  $\text{TC}^-$  and the  $\text{Ca}^{2+}$  interlayer cations.



**Figure 7.2.** Comparison between the experimental uptake adsorbed and the predicted uptake adsorbed with the EFM (a), ELM (b) and MRPM (c) isotherms for the adsorption of TC and Cd(II) on Bent at  $\text{pH} = 3$ .



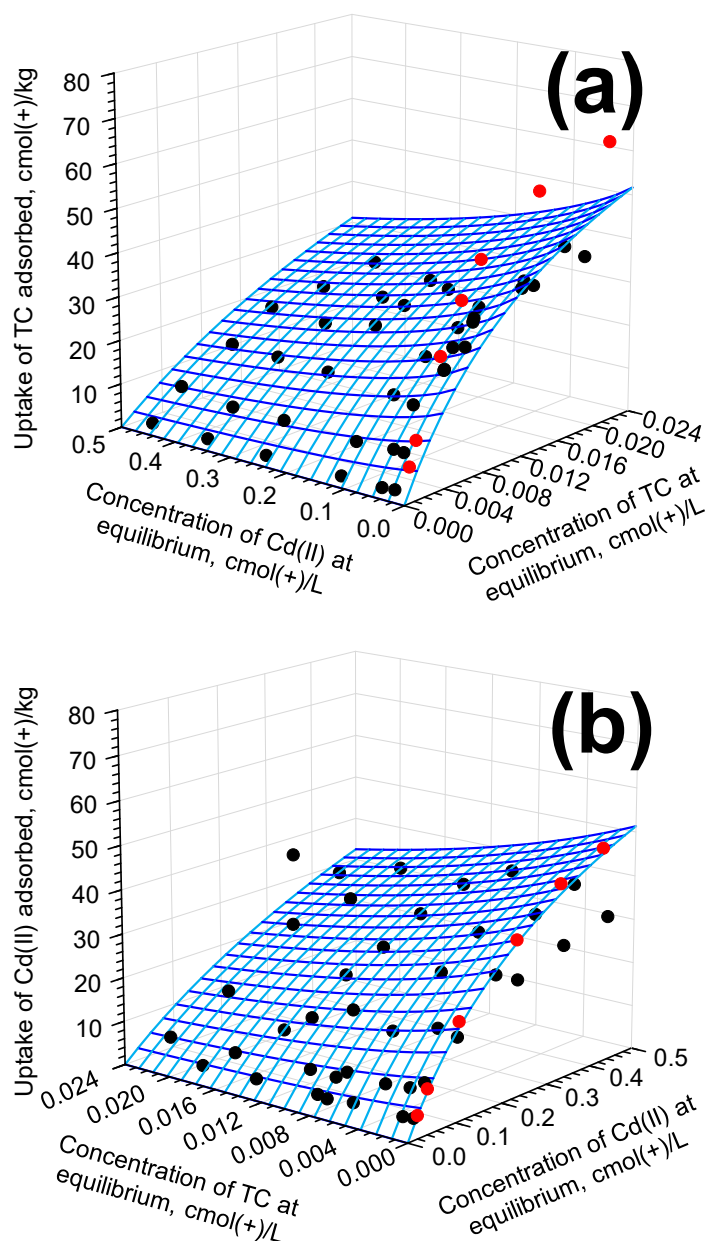


**Figure 7.3.** Single adsorption isotherms of TC (a) and Cd(II) (b) on Bent at  $T = 25$  °C and pH of 3 and 7. The lines represent the Langmuir isotherm.

The single adsorption isotherms of Cd(II) on Bent are depicted in Figure 7.3 (b), revealing a maximum adsorption capacity of 55.1 cmol(+)/kg (61.9 mg/g) at pH = 7, with a slight decrease as the solution pH increases. Diverse studies have identified electrostatic attractions and cation exchange as the predominant mechanisms in Cd(II) adsorption on Bent (Bedoui et al., 2008; Bosco et al., 2006; Mhamdi et al., 2014; Padilla-Ortega et al., 2014; Sen Gupta and Bhattacharyya, 2008). Ortiz-Ramos et al. (2022) estimated the surface charge distribution of Bent at pH 3 and 7, obtaining a Zeta potential of -20.6 and -29.6 mV, respectively. This indicates that the Bent surface is more negatively charged at pH 7 than at pH 3, explaining the higher adsorption capacity at pH = 7 due to enhanced electrostatic attraction.

### 7.3.3 Competitive adsorption isotherms of TC and Cd(II) in binary solution

Figure 7.4 displays three-dimensional graphs representing the experimental data of binary adsorption of TC and Cd(II) on Bent at  $T = 25$  °C and pH = 3. The red markers denote the experimental data points for the single adsorption equilibrium of TC or Cd(II) on Bent, while the blue surfaces depict the binary adsorption isotherms predicted by the MRPM model.



**Figure 7.4.** Binary adsorption isotherms on Bent at pH = 3 and T = 25 °C. Adsorption of TC in the presence of Cd(II) (a) and adsorption of Cd(II) in the presence of TC (b). The red markers represent the single adsorption isotherm, and the blue adsorption surfaces represent the MRPM isotherm.

In Figure 7.4 (a), the adsorption capacity of Bent for TC at various concentrations of Cd(II) is depicted. Notably, the presence of Cd(II) induces an

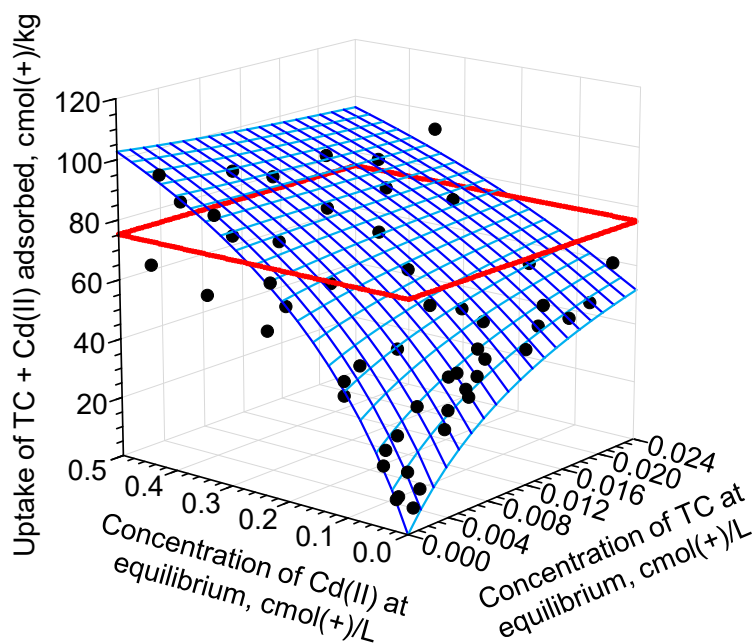
antagonistic effect on the adsorption capacity of Bent for TC, signifying a substantial decrease in the adsorption capacity towards TC as the equilibrium concentration of Cd(II) increases. For instance, at an equilibrium concentration of TC of 0.02 cmol(+)/L, the uptake of TC adsorbed was 63.5 cmol(+)/kg (282.2 mg/g), decreasing to 28.2 cmol(+)/kg (124.9 mg/g) as the equilibrium concentration of Cd(II) rises to 0.5 cmol(+)/L.

The effect of the presence of TC in the binary adsorption isotherm of Cd(II) on Bent at  $T = 25\text{ }^{\circ}\text{C}$  and  $\text{pH} = 3$  is illustrated in Figure 7.4 (b), also demonstrating an antagonistic effect on the adsorption capacity of Bent for Cd(II). The figure reveals a decrease in the uptake of Cd(II) adsorbed with an increase in the equilibrium concentration of TC. For example, at an equilibrium concentration of Cd(II) of 0.4 cmol(+)/L, the uptake of Cd(II) adsorbed was 47.8 cmol(+)/kg (53.7 mg/g), reducing to 28.2 cmol(+)/kg (31.6 mg/g) as the equilibrium concentration of TC increases to 0.024 cmol(+)/L.

The results demonstrate a clear antagonistic effect at  $\text{pH} = 3$ , indicating that the presence of TC diminishes the adsorption capacity of Bent for Cd(II) and vice versa. The interaction parameters estimated by the MRPM model were  $\eta_{\text{TC}} = 2.36$  and  $\eta_{\text{Cd}} = 1.07$ , revealing that Bent exhibits a higher affinity for TC than Cd(II) as  $\eta_{\text{TC}}$  is 2.2-fold higher than  $\eta_{\text{Cd}}$ . This assertion is supported by the following analysis: The MRPM predicted maximum adsorption capacities of Bent for Cd(II) and TC and  $\text{pH} = 3$  to be 47.9 (53.8 mg/g) and 50.2 cmol(+)/kg (223.1 mg/g), respectively. As the equilibrium concentration of both contaminants increases to 0.02 cmol(+)/L, the MRPM isotherm predicted a decrease in the adsorption capacities of Cd(II) and TC to 31.1 (34.9 mg/g) and 47.8 (212.4 mg/g) cmol(+)/kg, respectively. This signifies a reduction in the adsorption capacities of Bent for Cd(II) and TC by 35.1 and 4.7 %, respectively, in presence of the other contaminant with an equilibrium concentration of 0.02 cmol(+)/L. In simple terms, the presence of Cd(II) has a slight impact on reducing the adsorption capacity for TC, while the presence of TC significantly diminishes the capacity of Bent to adsorb Cd(II). This observation aligns with the findings of Segovia-Sandoval et al. (2019), who analyzed binary adsorption isotherms of metronidazole and Pb(II) on

commercial activated carbon. They observed a competitive effect in the adsorption capacities of metronidazole and Pb(II) and concluded that activated carbon exhibited a higher affinity for metronidazole than Pb(II).

The observed antagonistic effect in the binary adsorption isotherms of TC and Cd(II) on Bent can be elucidated as follows. At pH = 3, the presence of cationic species  $TC^+$  and the cation  $Cd^{2+}$  in the solution leads to potential competition between these contaminants for the same cationic sites located on the negatively charged surface of Bent. In Figure 7.5, the total uptake of TC and Cd(II) adsorbed on Bent at pH = 3 is illustrated, demonstrating a consistent value near 90 cmol(+)/kg as the equilibrium concentration of both contaminants increases. Additionally, the total uptake adsorbed is 1.2-fold higher than the cation exchange capacity of Bent, represented by the red line. These findings suggest that the adsorption of TC and Cd(II) on Bent at pH = 3 occurs through similar interactions and on the same adsorption sites, thereby fostering competition for the cationic exchange sites.

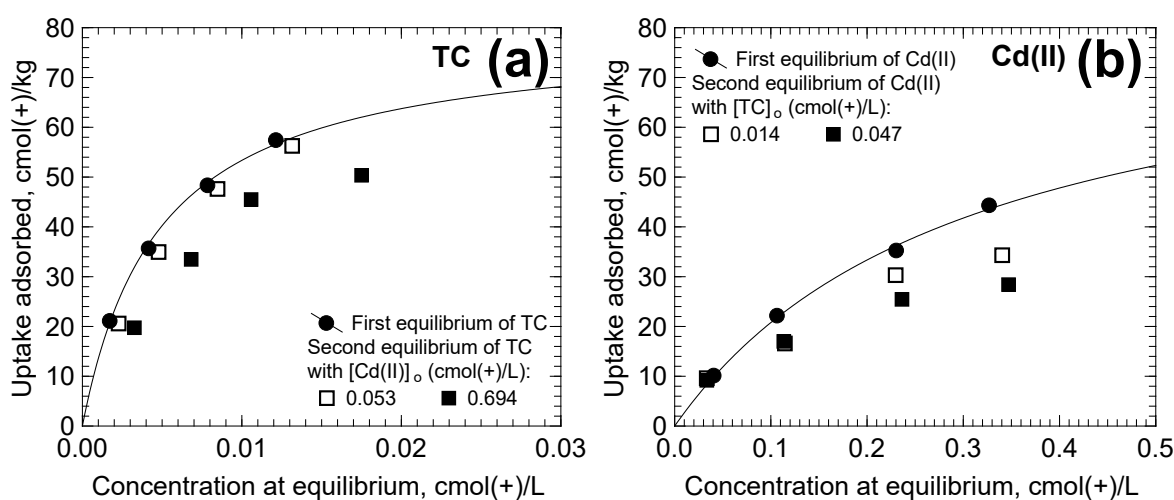


**Figure 7.5.** Total uptake of TC and Cd(II) adsorbed on Bent at pH = 3 and T = 25 °C. The adsorption surface represents the prediction with the MRPM isotherm. The red line depicts the cation exchange capacity, 75 cmol(+)/kg.

The displacement experiments of the adsorption equilibrium of TC by the adsorption of Cd(II) and the displacement of the adsorption equilibrium of Cd(II) by the adsorption of TC at pH = 3 are depicted in Figure 7.6. In Figure 7.6 (a), the single adsorption isotherm of TC on Bent at pH = 3 is presented, referred to as the first adsorption equilibrium, as initially only TC was present in the solution. The displacement or desorption of TC adsorbed on Bent begins when an aliquot of Cd(II) solution is added with a known initial concentration, causing TC to be displaced by Cd(II) and achieving a second adsorption equilibrium of TC, dependent on the initial concentration of Cd(II). The figure reveals that the uptake of TC adsorbed in the first equilibrium decreases as the initial concentration of Cd(II) increases, indicating desorption of TC adsorbed as a function of the initial concentration of Cd(II). The second adsorption equilibrium with an initial concentration of Cd(II) of 0.053 cmol(+)/L is slightly lower than the first adsorption equilibrium, but with an initial concentration of Cd(II) of 0.694 cmol(+)/L, the second adsorption equilibrium of TC notably decreases. For example, at an equilibrium concentration of TC of 0.012 cmol(+)/L, the uptake of TC adsorbed in the first equilibrium was 57.5 cmol(+)/kg (255.5 mg/g), while in the second adsorption equilibrium, it was 56.3 (250.2 mg/g) and 50.5 (224.4 mg/g) cmol(+)/kg with initial concentrations of Cd(II) of 0.053 and 0.694 cmol(+)/L, respectively. These results indicate that Cd(II) with initial concentrations of 0.053 and 0.694 cmol(+)/L displaced 2.1 and 12.2 % of the uptake of TC adsorbed in the first equilibrium, respectively.

In Figure 7.6 (b), the first and second adsorption equilibrium of Cd(II) on Bent at different initial concentrations of TC are illustrated. It was observed that Cd(II) desorbs as a function of the initial concentration of TC, as the second adsorption equilibrium decreases with increasing initial concentration of TC. For instance, at an initial concentration of Cd(II) of 0.33 cmol(+)/L, the uptake adsorbed in the first equilibrium was 44.3 cmol(+)/kg (49.8 mg/g), and in the second adsorption equilibrium, it was 34.5 (38.7 mg/g) and 28.6 (32.1 mg/g) cmol(+)/kg with initial concentrations of TC of 0.014 and 0.047 cmol(+)/L, respectively. This indicates that TC displaced 22.1 and 35.3 % of Cd(II) adsorbed on Bent, respectively, demonstrating that adsorption of TC and Cd(II)

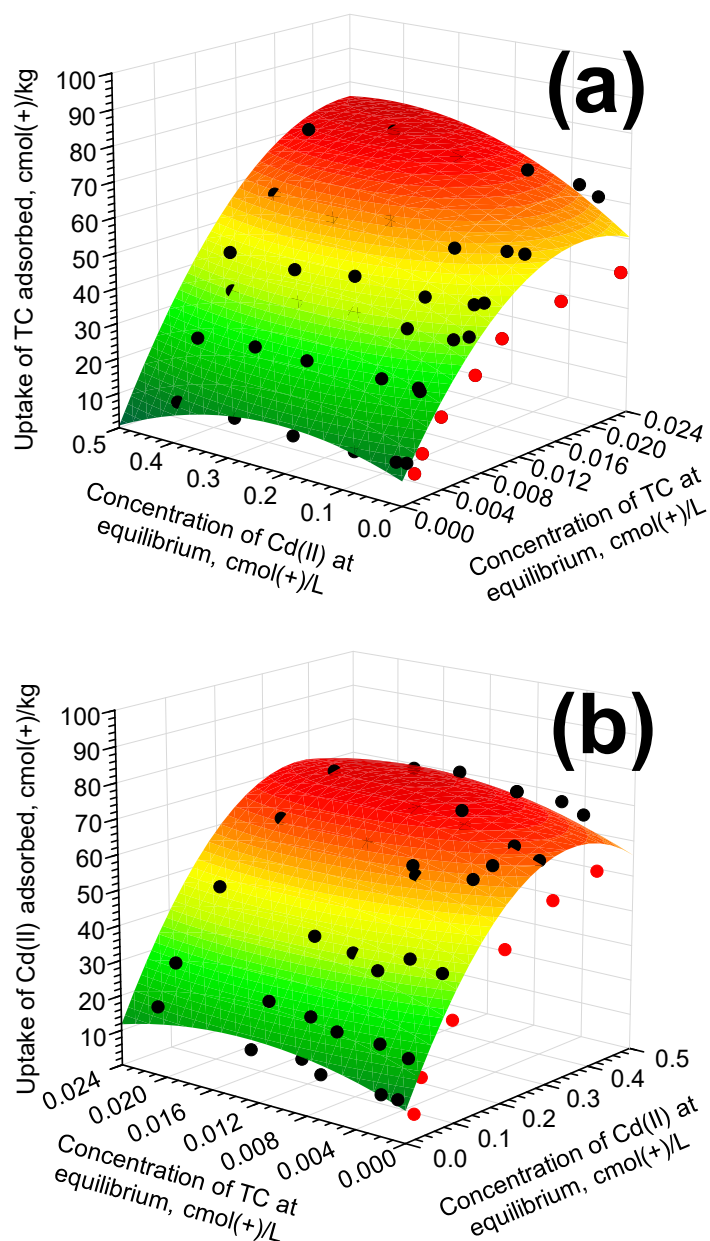
on Bent occurs on the same adsorption sites, promoting a competitive effect, and that Bent has a higher affinity for TC. A study investigating the competitive adsorption of the antibiotics metronidazole and dimetridazole on granular and fiber-type activated carbon observed a decreased in the uptake of adsorbed antibiotics in the presence of the other, concluding that the adsorption of both antibiotics is independent of carbon type. The competitive effect is attributed to the chemical properties of nitroimidazoles, as both antibiotics adsorb on the same adsorption sites and exhibit similar interactions (Carrales-Alvarado et al., 2018).



**Figure 7.6.** Displacement of adsorption equilibrium of TC on Bent by adsorption of Cd(II) (a) and displacement of adsorption equilibrium of Cd(II) on Bent by adsorption of TC (b) at pH = 3 and T = 25 °C. The lines represent the Langmuir isotherm.

### 7.3.4 Cooperative adsorption isotherms of TC and Cd(II) in binary solution

In Figure 7.7, the experimental data of binary adsorption of TC and Cd(II) on Bent at T = 25 °C and pH = 7 are illustrated. It is noteworthy that the adsorption capacity for TC significantly increased with an increase in the concentration of Cd(II) at equilibrium, and vice versa. In other words, an evident synergistic or cooperative effect is observed, rather than a competitive effect.



**Figure 7.7.** Binary adsorption isotherms on Bent at pH = 7 and T = 25 °C. Adsorption of TC in the presence of Cd(II) (a) and adsorption of Cd(II) in the presence of TC (b). The red markers represent the single adsorption isotherm, and the surfaces represent a polynomial contour plot.

The surfaces in the figure represent a contour plot but do not correspond to any of the multicomponent adsorption isotherm models previously described. This

discrepancy arises because these models, namely SRS, EFM and MRPM, failed to accurately interpret the cooperative effect observed in the binary adsorption system. This limitation stems from the fact that these models are derived from the Freundlich and Redlich-Peterson isotherms, while the experimental data exhibited behavior akin to the Langmuir isotherm. Furthermore, attempts to fit the data using MLM and ELM models proved unsatisfactory, as these models are constrained by the single adsorption capacities of TC and Cd(II) on Bent, which are significantly lower than their adsorption capacities in the binary solution.

In Figure 7.7 (a), it is evident that the adsorption capacity of Bent for TC significantly increased with an escalating concentration of Cd(II) at equilibrium. Specifically, at an equilibrium concentration of TC of 0.02 cmol(+)/L, the uptake of TC adsorbed was 41.2 cmol(+)/kg (183.1 mg/g), rising to 74.0 cmol(+)/kg (328.8 mg/g) as the concentration of Cd(II) at equilibrium increased to 0.5 cmol(+)/L. This indicates that the adsorption capacity of Bent for TC increases by a factor of 1.79 in the presence of Cd(II). Figure 7.7 (b) illustrates the adsorption of Cd(II) in the presence of TC, revealing an increase in adsorption capacity as the equilibrium concentration of TC rises to 0.024 cmol(+)/L. For instance, at an equilibrium concentration of Cd(II) of 0.04 cmol(+)/L, the uptake of Cd(II) adsorbed was 55.1 cmol(+)/kg (61.9 mg/g), escalating to 73.8 cmol(+)/kg (82.9 mg/g) as the equilibrium concentration of TC increased to 0.024 cmol(+)/L, representing 1.3 times increase in the adsorption capacity of Bent for Cd(II). In a related study, Martínez-Costa et al. (2018) investigated the adsorption capacity of organobentonite for sulfamethoxazole and Cd(II) in a binary solution, observing a significant increase in the adsorption capacity for Cd(II) in the presence of sulfamethoxazole, while the adsorption capacity for sulfamethoxazole remained unchanged with the presence of Cd(II).

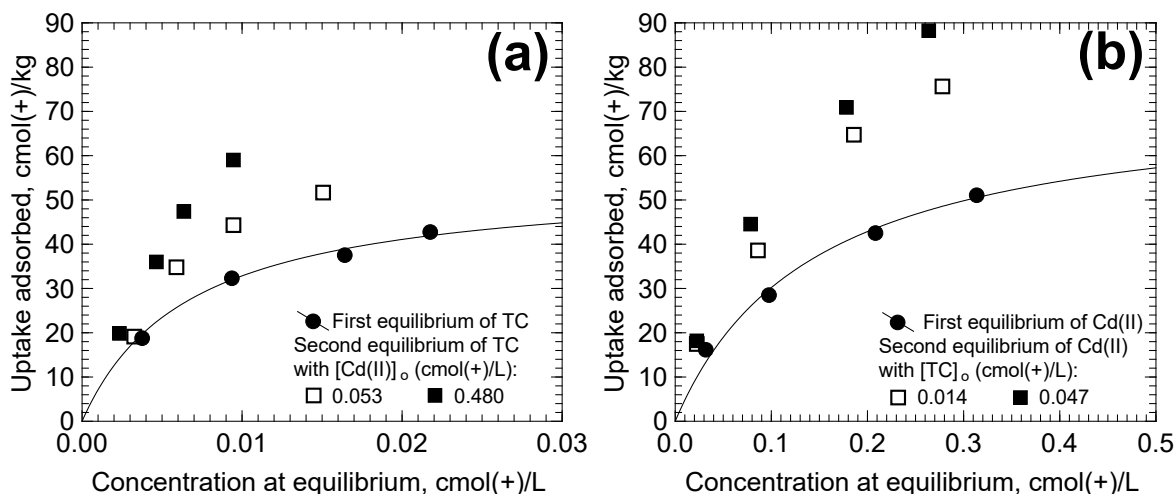
The observed cooperative effect in the binary adsorption isotherms of TC and Cd(II) on Bent at pH = 7 can be explained as follows. At pH = 7, both the negatively charged species TC<sup>-</sup> and the Cd<sup>2+</sup> cation coexist in the solution. Recent findings, as reported by Pulicharla et al. (2017), highlight that TC, when in its negative form, exhibits heightened electron density within the phenolic-diketone functional group. This



enhanced electron density serves as a facilitator for the formation of coordination complexes with diverse divalent cations, among which the  $\text{Cd}^{2+}$  cation is included. Therefore, the results suggest that the synergy in the capacity of Bent to adsorb TC and Cd(II) in the binary solution arises from an additional mechanism beyond cation exchange. In this mechanism, TC and Cd(II) can be adsorbed on the same sites and form coordination complexes. These findings align with other studies demonstrating that the adsorption capacity of different minerals for TC can be enhanced in the presence of divalent metal cations through the formation of coordination complexes and the cation-bridging effect (Hsu et al., 2018; Jia et al., 2008; Wan et al., 2010; Wang et al., 2008; Zhao et al., 2013).

The displacement experiments of TC adsorbed by the adsorption of Cd(II) at  $T = 25\text{ }^{\circ}\text{C}$  and  $\text{pH} = 7$  are presented in Figure 7.8 (a). In contrast to the observed results of displacement experiments at  $\text{pH} = 3$ , the experimental data did not demonstrate a displacement of TC adsorbed as a function of the initial concentration of Cd(II). Instead, it revealed that TC present in the solution during the first adsorption equilibrium was adsorbed incrementally with an increase in the initial concentration of Cd(II), reaching a second adsorption equilibrium above the adsorption isotherm of the first equilibrium. Specifically, at a concentration of TC at equilibrium of  $0.0094\text{ cmol(+)}/\text{L}$ , the second adsorption equilibrium was 1.85 times higher than the first adsorption equilibrium when the Cd(II) solution at an initial concentration of  $0.48\text{ cmol(+)}/\text{L}$  was added. Figure 7.8 (b) represents the displacement experiment of Cd(II) adsorbed by adsorption of TC at  $T = 25\text{ }^{\circ}\text{C}$  and  $\text{pH} = 7$ , showing similar results. At a concentration of Cd(II) at equilibrium of  $0.26\text{ cmol(+)}/\text{L}$ , the second adsorption equilibrium of Cd(II) with an initial concentration of TC of  $0.047\text{ cmol(+)}/\text{L}$  was  $88.3\text{ cmol(+)}/\text{kg}$  ( $99.2\text{ mg/g}$ ), resulting in 1.72 times higher than the first adsorption equilibrium of Cd(II). These findings indicate that there is no competition between TC and Cd(II) for the same adsorption sites, but rather a cooperative effect. This cooperative effect can be attributed to the distinct mechanisms through which TC and Cd(II) adsorb. At  $\text{pH} = 7$ ,  $\text{TC}^{\pm}$  and  $\text{TC}^{-}$  species adsorb through weak physical interactions and complexation with the interlayer  $\text{Ca}^{2+}$  cation, respectively, while the  $\text{Cd}^{2+}$  cation adsorbs through cation exchange and

electrostatic attractions. The second adsorption equilibrium of TC and Cd(II) achieved above the first adsorption equilibrium provides further evidence of the formation of coordination complexes between TC and Cd(II). With TC present in the solution and with additions of Cd(II), a portion of TC forms complexes with the  $\text{Cd}^{2+}$  cation, promoting the simultaneous adsorption of TC and Cd(II) on the available adsorption sites. Zhao et al. (2019) investigated the binary adsorption of tetracycline and Cu(II) on graphene oxide and reduced graphene oxide and observed a cooperative effect in the adsorption capacity towards tetracycline. The authors concluded that tetracycline and Cu(II) form a complex that adsorbs on the adsorbent surface through a cation-bridging effect.

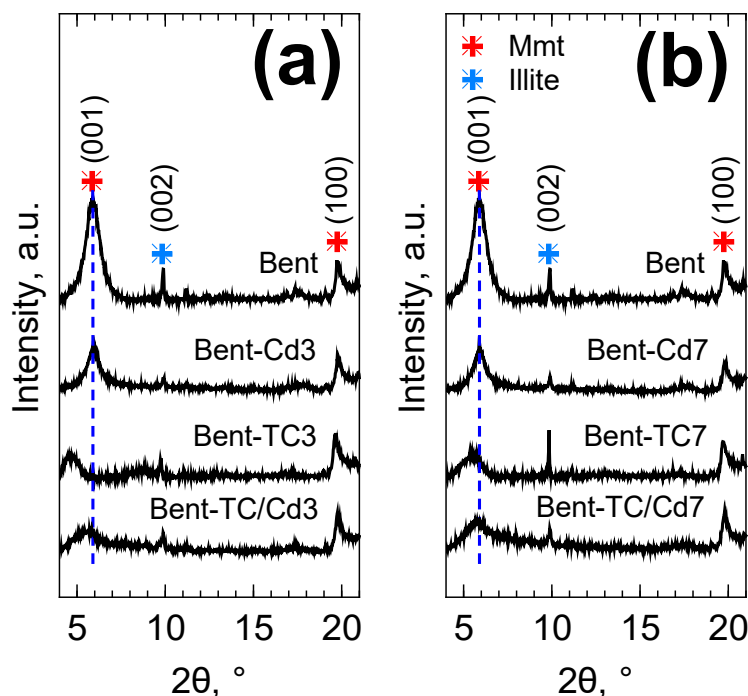


**Figure 7.8.** Displacement of adsorption equilibrium of TC on Bent by adsorption of Cd(II) (a) and displacement of adsorption equilibrium of Cd(II) on Bent by adsorption of TC (b) at pH = 7 and T = 25 °C. The lines represent the Langmuir isotherm.

### 7.3.5 XRD analysis of bentonite with TC and Cd(II) adsorbed

Figure 7.9 presents the X-ray patterns of Bent, Bent-Cd, Bent-TC, and Bent-TC/Cd at pH 3 and 7, typical of a smectite clay (Alabarse et al., 2011; Greene-Kelly, 1955). Three reflections were detected at positions 5.89, 9.80, and 19.72 ° (2 $\theta$ ) in Bent, corresponding to the crystal planes with Miller indices (001), (002), and (100), respectively. Planes (001) and (100) belong to the montmorillonite phase, the primary

crystalline phase of Bent, while plane (002) is attributed to the presence of illite in the samples. No feldspars or quartz were detected in the 4 to 21 ° (2 $\theta$ ) range.



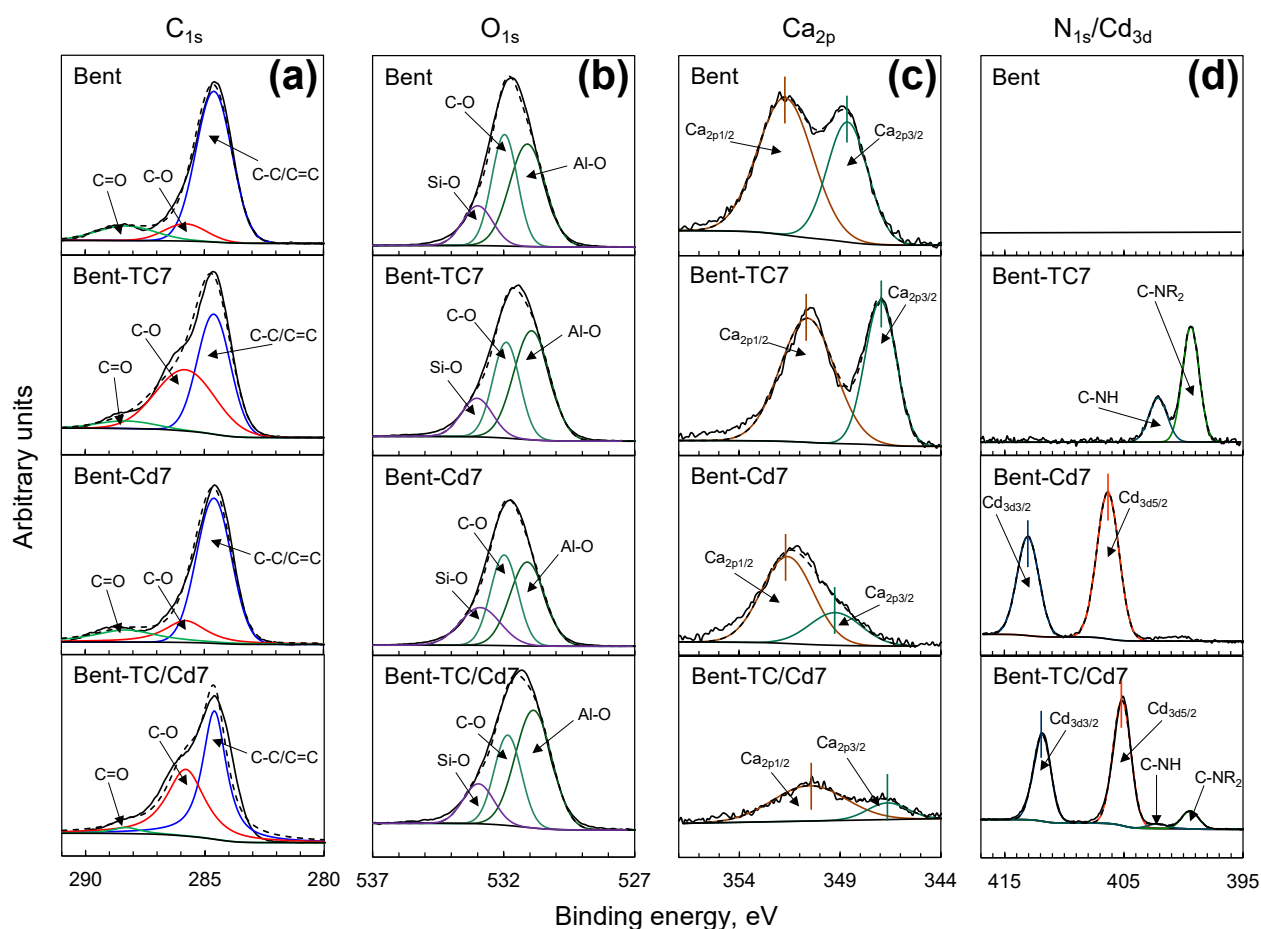
**Figure 7.9.** X-ray patterns of Bent and Bent saturated with Cd (Bent-Cd) and TC (Bent-TC) in a single solution and TC y Cd(II) (Bent-TC/Cd) in a binary solution at pH = 3 (a) and pH = 7 (b).

The basal distance of plane (001) forms the thickness of the trilaminar block and the interlayer space of Bent, measuring 1.50 nm. Moore and Hower (1986) estimated the thickness of the trilaminar block of a smectite to be 0.96 nm, suggesting an interlayer distance in Bent of 0.54 nm, attributed to water molecules surrounding interlayer  $\text{Ca}^{2+}$  cations in a hydration sphere. X-ray patterns of Bent-Cd, Bent-TC, and Bent-TC/Cd obtained at pH = 3 are shown in Figure 7.9 (a), with estimated  $d_{001}$  values of 1.49, 1.89, and 1.55 nm, corresponding to interlayer spaces of 0.53, 0.93, and 0.59 nm, respectively. It is observed that the Bent-Cd3 sample did not show a significant change in the interlayer space due to the individual adsorption of Cd(II), related to the hydrated ionic sizes of  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$ . The hydrated ionic size of  $\text{Cd}^{2+}$  is 0.426 nm, and that of  $\text{Ca}^{2+}$  is 0.412 nm (Nightingale, 1959). Thus,  $\text{Cd}^{2+}$  can easily replace interlayer

$\text{Ca}^{2+}$  cations through cation exchange reactions without causing a noticeable variation in the basal distance  $d_{001}$ , as they have very similar hydrated ionic sizes. These results are consistent with other studies (Liu et al., 2018; Wu et al., 2009). The Bent-TC3 sample exhibited a shift to the reflection of plane (001) to smaller angles, indicating an increase in the interlayer space due to the adsorption of TC in the individual system up to 0.93 nm. According to the dimensions of TC ( $X = 1.38$  nm,  $Y = 0.81$  nm,  $Z = 0.69$  nm), the interlayer space in Bent-TC3 is wide enough for TC to intercalate in a parallel orientation on the XZ plane. The X-ray pattern of the binary sample Bent-TC/Cd3 showed a contraction of the Bent layers compared to the Bent-TC3 sample, that is, the interlayer space decreased from 0.93 to 0.59 nm. This effect in the Bent-TC/Cd3 sample is associated with the competitive effect between TC and Cd(II) for the same adsorption sites, significantly reducing the adsorption capacity for TC, and consequently, the interlayer space. X-ray patterns obtained at pH = 7 for the Bent-Cd, Bent-TC, and Bent-TC/Cd samples are shown in Figure 7.9 (b). The Bent-Cd7 sample did not present any shift of the reflection at (001), consistent with the results obtained in the Bent-Cd3 sample. On the other hand, a shift of the reflection (001) in Bent-TC7 to smaller angles was observed, indicating an increase in the interlayer space. The  $d_{001}$  value was 1.62 nm, and the interlayer space was 0.66 nm, suggesting a parallel intercalation on the XY plane of the TC molecule. The X-ray patterns of the Bent-TC/Cd7 sample yielded a  $d_{001}$  value of 1.55 nm and an interlayer space of 0.59 nm, that is, a shift to larger angles compared to the Bent-TC7 sample, indicating a contraction of the Bent layers. In a previous study, it was concluded that the adsorption of TC on Bent at pH = 7 occurs in the interlayer space but also on the external surface of Bent. Thus, the decrease in the interlayer space in Bent-TC/Cd7 can be explained as follows. The adsorbed uptake of TC in the Bent-TC7 and Bent-TC/Cd7 samples is 34.5 and 37.0 cmol(+)/kg, respectively, showing that the adsorption capacity for TC increased due to the cooperative effect with Cd(II). Therefore, despite the increase in the uptake of TC adsorbed in Bent, the decrease in  $d_{001}$  can be associated with TC and Cd(II) adsorbing synergistically as a coordination complex on the external surface of Bent, causing the contraction of the clay layers.

### 7.3.6 XPS analysis of bentonite with TC and Cd(II) adsorbed

To demonstrate the formation of coordination complexes during the cooperative adsorption of TC and Cd(II) on Bent at pH = 7, XPS analyses were conducted on the Bent, Bent-TC7, Bent-Cd7, and Bent-TC/Cd7 samples. The XPS spectra, illustrated in Figure 7.10, provide insights into the chemical composition of these samples across selected spectral regions, including C<sub>1s</sub>, O<sub>1s</sub>, Ca<sub>2p</sub>, N<sub>1s</sub> and Cd<sub>3d</sub>. The corresponding data for these samples are summarized in Table 7.3, while Table 7.4 presents the surface chemical composition derived from XPS analyses.



**Figure 7.10.** XPS patterns of the C<sub>1s</sub> (a), O<sub>1s</sub> (b), Ca<sub>2p</sub> (c) and N<sub>1s</sub>/Cd<sub>3d</sub> (d) spectral regions of Bent and Bent saturated with Cd (Bent-Cd7) and TC (Bent-TC7) in a single solution and TC y Cd(II) (Bent-TC/Cd7) in a binary solution at pH = 7.

**Table 7.3.** XPS data of the Bent, Bent-TC7, Bent-Cd7 and Bent-TC/Cd7 samples.

| Sample      | C <sub>1s</sub> |       |            | O <sub>1s</sub> |       | Ca <sub>2p</sub> |       | N <sub>1s</sub> |       | Cd <sub>3d</sub> |       |
|-------------|-----------------|-------|------------|-----------------|-------|------------------|-------|-----------------|-------|------------------|-------|
|             | BE (eV)         | %Peak | Assignment | BE (eV)         | %Peak | BE (eV)          | %Peak | BE (eV)         | %Peak | BE (eV)          | %Peak |
| Bent        | 284.6           | 77.2  | C-C/C=C    | 531.1           | 47.5  | 351.7            | 60.6  |                 |       |                  |       |
|             | 285.8           | 10.4  | C-O        | 532.0           | 37.1  | 348.6            | 39.4  |                 |       |                  |       |
|             | 288.3           | 12.4  | C=O        | 533.0           | 15.5  |                  |       |                 |       |                  |       |
| Bent-TC7    | 284.6           | 49.4  | C-C/C=C    | 530.9           | 50.9  | 350.6            | 59.9  | 402.1           | 29.4  |                  |       |
|             | 285.8           | 45.3  | C-O        | 531.9           | 35.5  | 347.0            | 40.1  | 399.4           | 70.6  |                  |       |
|             | 288.3           | 5.4   | C=O        | 533.0           | 15.6  |                  |       |                 |       |                  |       |
| Bent-Cd7    | 284.6           | 68.6  | C-C/C=C    | 531.1           | 42.2  | 351.6            | 72.5  |                 |       | 413.0            | 39.9  |
|             | 285.8           | 17.0  | C-O        | 532.0           | 35.8  | 349.2            | 27.5  |                 |       | 406.3            | 60.1  |
|             | 288.3           | 14.4  | C=O        | 532.9           | 22.1  |                  |       |                 |       |                  |       |
| Bent-TC/Cd7 | 284.6           | 53.1  | C-C/C=C    | 530.9           | 53.7  | 350.5            | 79.6  | 402.2           | 22.3  | 411.9            | 40.4  |
|             | 285.8           | 44.0  | C-O        | 531.8           | 30.8  | 346.7            | 20.4  | 399.4           | 77.7  | 405.2            | 59.6  |
|             | 288.3           | 2.9   | C=O        | 533.0           | 15.5  |                  |       |                 |       |                  |       |

**Table 7.4.** Surface chemical composition of Bent, Bent-TC7, Bent-Cd7 and Bent-TC/Cd7 samples obtained by XPS.

| Sample      | C <sub>XPS</sub><br>(%) | O <sub>XPS</sub><br>(%) | Ca <sub>XPS</sub><br>(%) | N <sub>XPS</sub><br>(%) | Cd <sub>XPS</sub><br>(%) | Al <sub>XPS</sub><br>(%) | Si <sub>XPS</sub><br>(%) | Na <sub>XPS</sub><br>(%) | Mg <sub>XPS</sub><br>(%) | K <sub>XPS</sub><br>(%) |
|-------------|-------------------------|-------------------------|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|
| Bent        | 25.44                   | 51.66                   | 1.23                     | -                       | -                        | 5.03                     | 14.52                    | 0.19                     | 1.21                     | 0.72                    |
| Bent-TC7    | 57.32                   | 29.15                   | 1.01                     | 3.16                    | -                        | 2.32                     | 6.60                     | 0.10                     | 0.34                     | 0.00                    |
| Bent-Cd7    | 25.23                   | 52.42                   | 0.69                     | -                       | 1.47                     | 5.03                     | 13.26                    | 0.31                     | 1.26                     | 0.33                    |
| Bent-TC/Cd7 | 66.31                   | 21.82                   | 0.29                     | 3.91                    | 2.73                     | 1.30                     | 3.44                     | 0.00                     | 0.19                     | 0.00                    |

The deconvolution of the C<sub>1s</sub> spectral region is shown in Figure 7.10 (a) and can be resolved into three peaks: C-C/C=C (284.6 eV), C-O (285.8 eV) and C=O (288.3 eV). Notably, differences are evident in the Bent-TC7 and Bent-TC/Cd7 samples, where the intensity of the peak corresponding to C-O bond increases. Moreover, an elevated carbon content is observed in these samples, rising from 25.44 % in Bent to 57.32 % and 66.31 % in Bent-TC7 and Bent-TC/Cd7, respectively. In the O<sub>1s</sub> spectral region (Figure 7.10 (b)), no differences were observed in the samples. The peaks corresponding to the N<sub>1s</sub> spectral region (Figure 7.10 (d)) appear in both samples and can be attributed to the bonds C-NH (402.1 eV) of the amide group and C-NR<sub>2</sub> (399.4

eV) of the dimethylamino group of TC. These observations substantiate the presence of TC on the surface of Bent in both single and binary solutions, as these changes are not observed in the Bent-Cd7 sample. Conversely, the  $Cd_{3d}$  spectral region (Figure 7.10 (d)) in both the Bent-Cd7 and Bent-TC/Cd7 samples exhibits peaks corresponding to  $Cd_{3d3/2}$  and  $Cd_{3d5/2}$ , confirming the presence of Cd(II) in both single and binary solutions.

Figure 7.10 (c) shows the peaks  $Ca_{2p1/2}$  (351.7 eV) and  $Ca_{2p3/2}$  (348.6 eV) of the  $Ca_{2p}$  spectral region and shifts to lower binding energies were observed in the Bent-TC7 sample due to the adsorption of TC in a single solution through complexation with  $Ca^{2+}$  interlayer cation. In the Bent-Cd7 sample, these shifts were not registered, but it is noted that the calcium content decreased from 1.23 to 0.69 % due to cationic exchange between  $Ca^{2+}$  interlayer cation and  $Cd^{2+}$  in single solution. In the Bent-TC/Cd7 sample, both shifts to lower binding energies and a reduction in calcium content to 0.29 % were registered, demonstrating the presence of both adsorption mechanisms in the binary solution: cationic exchange of the  $Ca^{2+}$  interlayer cation and complexation with the remaining  $Ca^{2+}$  cations.

In the Bent-TC/Cd7 sample, nitrogen and cadmium content increased compared to the Bent-TC7 and Bent-Cd7 samples, respectively. For instance, nitrogen content increased from 3.16 to 3.91 %, and the cadmium content from 1.47 to 2.73 %. These results indicate that the presence of both contaminants in solution promotes their adsorption through a cooperative effect, in comparison with single solutions of both contaminants.

Additionally, the binding energies of the  $Cd_{3d3/2}$  and  $Cd_{3d5/2}$  peaks in the  $Cd_{3d}$  spectral region (Figure 7.10 (d)) shifted to lower values in the presence of TC.  $Cd_{3d3/2}$  shifted from 413 eV to 411.9 eV, and  $Cd_{3d5/2}$  from 406.3 eV to 405.2 eV, suggesting that Cd(II) is in a reduced state in the presence of TC. In the Bent-TC/Cd7 sample, the high electron density originating from the resonance of the double bond  $C=O$  of the C ring of TC, corresponding to the phenolic diketone functional group, generates a negative charge on the resonant ring. This indicates that the functional group acts as an electron donor, interacting with Cd(II) and complexing through the oxygen atoms.

Previously, it was elucidated that electrostatic attractions contribute to the adsorption of Cd(II) on the Bent surface. This implies that Cd(II) can complex with a TC molecule on one side, and with cationic sites of the Bent surface on the other side, forming a ternary complex Bent-Cd(II)-TC. The bridging effect presented by Cd(II) generates more adsorption sites for TC molecules, enhancing the adsorption capacity for both contaminants.

#### 7.4 Conclusions

The binary adsorption mechanisms of TC and Cd(II) on Bent are pH-dependent, given the variations in TC and Cd(II) species and the surface charge of Bent at different pH values. At pH = 3, a competitive or antagonistic effect is observed in the adsorption capacities of TC and Cd(II), whereas at pH = 7, a cooperative or synergistic effect is evident.

At pH = 3, the TC<sup>+</sup> and Cd<sup>2+</sup> species are present, and the surface of Bent is negatively charged. The adsorption of TC<sup>+</sup> and Cd<sup>2+</sup> occurs in the interlayer space of Bent and is governed by electrostatic interactions between the cationic species of TC and Cd(II) and the negatively charged surface of Bent, along with cation exchange with the interlayer cations of Bent. In this scenario, TC and Cd(II) compete for the same cationic sites located on the negatively charged surface of Bent, leading to a significant decrease in the adsorption capacity for both TC and Cd(II).

At pH = 7, the solution contains the TC<sup>±</sup>/TC<sup>-</sup> and Cd<sup>2+</sup> species, and a cooperative adsorption takes place through complexation mechanisms. The phenolic diketone group of TC exhibits resonance of the double bond C=O in the C ring, creating a high electron density that results in a negative charge on the resonant ring. This electron density is stabilized by forming a coordination complex with the Cd<sup>2+</sup> cation. Adsorption occurs on the external surface of Bent via a cationic bridge, significantly increasing the capacity of Bent to adsorb both TC and Cd(II).



# CHAPTER

# 8

**EXPLORING ADSORPTIVE  
BEHAVIOR OF CATIONIC, ANIONIC,  
ZWITTERIONIC AND NEUTRAL  
PHARMACEUTICALS IN AQUEOUS  
SOLUTION ON  
HEXADECYLTRIMETHYLAMMONIUM  
BROMIDE-MODIFIED  
ORGANOBENTONITE**

## **8.1 Introduction**

Clays, a class of natural non-toxic minerals, stand out for their widespread availability, easy extraction, and cost-effectiveness, distinguishing them from other materials. Their exceptional characteristics, including high specific surface area, porosity, negative charge, colloidal behavior, surface functional groups, and cation exchange and swelling capacity, make them invaluable as adsorbents for removing heavy metals from water (Chai et al., 2020; Es-sahbany et al., 2021; Hussain and Ali, 2021; Liu et al., 2018; Padilla-Ortega et al., 2020; Wu et al., 2009).

Bentonite, a type of clay rich the montmorillonite phase and classified within the smectite group, is renowned for its distinctive properties. Its layered structure comprises interconnected tetrahedral silica (T) and octahedral alumina or magnesia (O) sheets, forming a trilaminar block type T:O:T configuration. Within these sheets, isomorphous substitutions of cations by lower-charged atoms create an excess of negative charge on the surface, balanced by exchangeable and hydratable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  residing in the interlayer space. These cations undergo outer-sphere hydration, whereby they are entirely enveloped by water molecules, establishing weak bonds with the clay surface.

Despite their characteristics as adsorbents, research has concluded that bentonite often falls short in effectively adsorbing organic pollutants, particularly pharmaceutical compounds, prevalent hazardous emerging contaminants in water systems. For instance, Thiebault and Boussafir (2019) found a low adsorption capacity of 10.2 mg/g for diazepam on montmorillonite at pH = 7.5, while Vallova et al. (2022) observed incomplete removal of analgesics such as paracetamol, diclofenac and ibuprofen from aqueous solutions. These studies conclude that the negative and hydrophilic surface of bentonite inhibits the adsorption capacity of pharmaceutical compounds.

Clay modification with organic compounds provides a promising approach to create organoclays, characterized by highly hydrophobic and organophilic surfaces, thereby enhancing the potential for increased adsorption capacity towards pharmaceuticals. Various agents, including Gemini surfactants (Shen and Gao, 2019),

cationic surfactants (Leyva-Ramos et al., 2021), amino acids (Imanipoor et al., 2021), phospholipids (Liu et al., 2017) and even polymeric macromolecules (Kausar et al., 2019) have been employed for clay modification. Among these, cationic surfactants, including hexadecyltrimethylammonium bromide, dodecyltrimethylammonium bromide and benzyltrimethylammonium bromide are frequently used for organoclay preparation.

Several studies have delved into the adsorption of pharmaceutical compounds on organoclays, yielding varied results. For instance, De Oliveira et al. (2017) examined the adsorption of diclofenac on organomontmorillonite modified with two different surfactants: benzyldimethyltetradecylammonium bromide (BDTA) and hexadecyltrimethylammonium bromide (HDTMA). They observed slight variations in diclofenac adsorption capacity depending on the surfactant employed. Materials prepared with BDTA and HDTMA showed diclofenac adsorption capacities of 56.3 and 44.4 mg/g, respectively. However, another study reported a much higher diclofenac adsorption capacity of 361.3 mg/g on HDTMA-modified bentonite (Martinez-Costa et al., 2018). In another recent investigation, the adsorption of paracetamol on organobentonites modified with different surfactants, both anionic (sodium dodecyl sulfate and dodecyl benzene sulfonic acid) and cationic (dodecyltrimethylammonium bromide and dodecylpyridinium chloride), was studied. The adsorption capacity was found to be contingent upon the type of ionic surfactant used. The organoclay modified with dodecyltrimethylammonium bromide showed the highest paracetamol adsorption capacity of 32.4 mg/g, while adsorption capacities decreased in the following order: dodecylpyridinium bromide > sodium dodecyl sulfate > dodecyl benzene sulfonic acid (Çalışkan Salihi et al., 2023). The hydrophobic effect exerted by the surfactant chains within the clay was identified as a significant factor influencing adsorption.

While numerous studies have concluded that organoclays exhibit high adsorption capacities for pharmaceutical compounds (França et al., 2020; Imanipoor et al., 2021; Malvar et al., 2020; Saitoh and Shibayama, 2016; Vallova et al., 2022; Zhang et al., 2021), contradictory results have also emerged where the organic modification of the clay fails to increase or even reduces the adsorption capacity. For example, Yang et al. (2020) found that organic modification did not significantly

enhance the adsorption the adsorption capacity of tetracycline on organovermiculite modified with the surfactant dodecyl dimethyl betaine (DDB). Similarly, Martínez-Costa et al. (2018) investigated the adsorption of sulfamethoxazole and trimethoprim on HDTMA-modified organobentonite, revealing that while the organobentonite exhibited a high individual adsorption capacity for sulfamethoxazole, it did not for trimethoprim. These contrasting results highlight the complexity of the adsorption process and emphasize the need for further investigation into the mechanisms governing adsorption on organoclays.

Chapter 8 aims to explore the adsorption behavior of pharmaceuticals with varying ionic nature, including cation chlorphenamine (CPA), anion sulfamethoxazole (SMX), zwitterion tetracycline (TC) and neutral carbamazepine (CBZ), on hexadecyltrimethylammonium bromide-modified organobentonite. These pharmaceuticals are challenging to remove through sewage treatment systems due to their low degradation rates, posing risks such as drug resistance and adverse effects on aquatic life. Organobentonite were prepared via a cation exchange reaction route and comprehensively characterized by N<sub>2</sub> physisorption, SEM, XRD, FT-IR, Zeta potential and thermogravimetric analysis. Adsorption isotherms of the pharmaceuticals were obtained to investigate the effect of solute ionic nature on adsorption capacity, while operating conditions, including pH, temperature and ionic strength were systematically examined. The chapter aims to elucidate adsorption mechanisms and mass transport mechanisms controlling the adsorption rate of pharmaceuticals on organobentonite.

## **8.2 Experimental methodology**

### **8.2.1 Preparation of hexadecyltrimethylammonium bromide-modified organobentonite**

The precursor bentonite (Bent) utilized for the preparation of organobentonite was obtained from a mineral deposit located in Mexico. The extraction and conditioning process is described in detail in Chapter 4. Organobentonite (OrganoBent) was prepared through a cation exchange reaction between bentonite and the cationic

surfactant hexadecyltrimethylammonium bromide (HDTMA). Initially, an HDTMA solution was prepared with an initial concentration of 80 mmol/L, exceeding the critical micellar concentration. Subsequently, a specific volume of this HDTMA solution was brought into contact with a predetermined mass of Bent, maintaining a volume/mass ratio of 120 mL/g, for a period of 7 days with constant agitation. Finally, the concentration at the beginning and at the end of the cation exchange experiment was quantified using an indirect colorimetric method involving the reaction of HDTMA with the dye Orange II, forming a colored compound. This compound was separated via liquid-liquid extraction using chloroform, and its absorbance was measured at a wavelength of 486 nm using a Shimadzu UV-Vis spectrophotometer, model 2600.

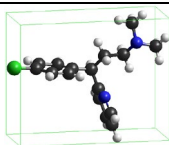
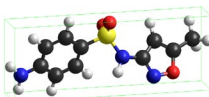
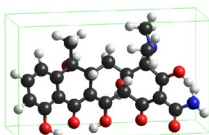
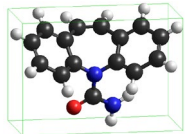
### **8.2.2 Characterization of the adsorbent materials**

The textural properties of Bent and OrganoBent were determined utilizing experimental data obtained from N<sub>2</sub> adsorption-desorption isotherms. N<sub>2</sub> adsorption and desorption were measured using a Micromeritics analyzer, model ASAP 2020. The morphology of the materials was examined using a JEOL scanning electron microscope, model JSM-6610LV, capturing secondary electron images at different magnifications, with an acceleration voltage of 10 kV. The surface charge distribution and the isoelectric point of the materials were determined following the procedure described in Chapter 4, Section 4.2.3, using a Malvern Zetameter, model Zetasizer 4, over a pH range from 2 to 12. X-ray patterns of the samples were obtained using a Rigaku X-ray diffractometer, model DMAX 2000, with the following operating conditions: Cu-K $\alpha$  radiation ( $\lambda = 0.15406$  nm), a current of 30 mA and a voltage of 30 kV. X-ray patterns were recorded in the range of 4 to 50 ° (2 $\theta$ ) at a scan rate of 1.8 °/min. Infrared spectra were acquired over the wavenumber range of 4000 to 400 cm<sup>-1</sup> using a Fourier-transform infrared spectrophotometer from Thermo-Scientific, model Nicolet iS10. Finally, thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves were generated using a Perkin Elmer thermogravimetric analyzer, model Pyris Diamond TGA/DTG, over a temperature range from 25 to 800 °C, with a heating rate of 10 °C/min.

### 8.2.3 Cationic, anionic, zwitterionic and neutral pharmaceutical compounds

The pharmaceutical compounds selected for the purpose of this research are as follows: chlorphenamine (CPA) (CAS: 113-92-8), sulfamethoxazole (SMX) (CAS: 723-46-6), tetracycline (TC) (CAS: 60-54-8) and carbamazepine (CBZ) (CAS: 298-46-4). These compounds were provided by Merck. The physicochemical properties of the pharmaceutical compounds are detailed in Table 8.1. Additionally, Figure 8.1 depicts their chemical species distribution diagrams at a total concentration of 0.5 mmol/L.

**Table 8.1.** Physicochemical properties of the pharmaceutical compounds.

| Pharmaceuticals                         | Ionic charge at pH = 7 | Molecular structure <sup>a</sup>                                                    | Molecular size <sup>a</sup> (nm) | Log D <sup>b</sup> | pK <sub>a</sub> <sup>c</sup> |
|-----------------------------------------|------------------------|-------------------------------------------------------------------------------------|----------------------------------|--------------------|------------------------------|
| Chlorphenamine (CPA)<br>M.W. = 274.79   | +                      |    | X = 1.11<br>Y = 0.91<br>Z = 0.49 | 1.15               | 4.00, 9.20                   |
| Sulfamethoxazole (SMX)<br>M.W. = 253.28 | -                      |  | X = 1.23<br>Y = 0.46<br>Z = 0.24 | 0.14               | 1.60, 5.70                   |
| Tetracycline (TC)<br>M.W. = 444.44      | +/-                    |  | X = 1.34<br>Y = 0.78<br>Z = 0.51 | -1.30              | 3.32, 7.78, 9.58             |
| Carbamazepine (CBZ)<br>M.W. = 236.27    | 0                      |  | X = 0.90<br>Y = 0.63<br>Z = 0.48 | 2.77               | 2.30, 13.90                  |

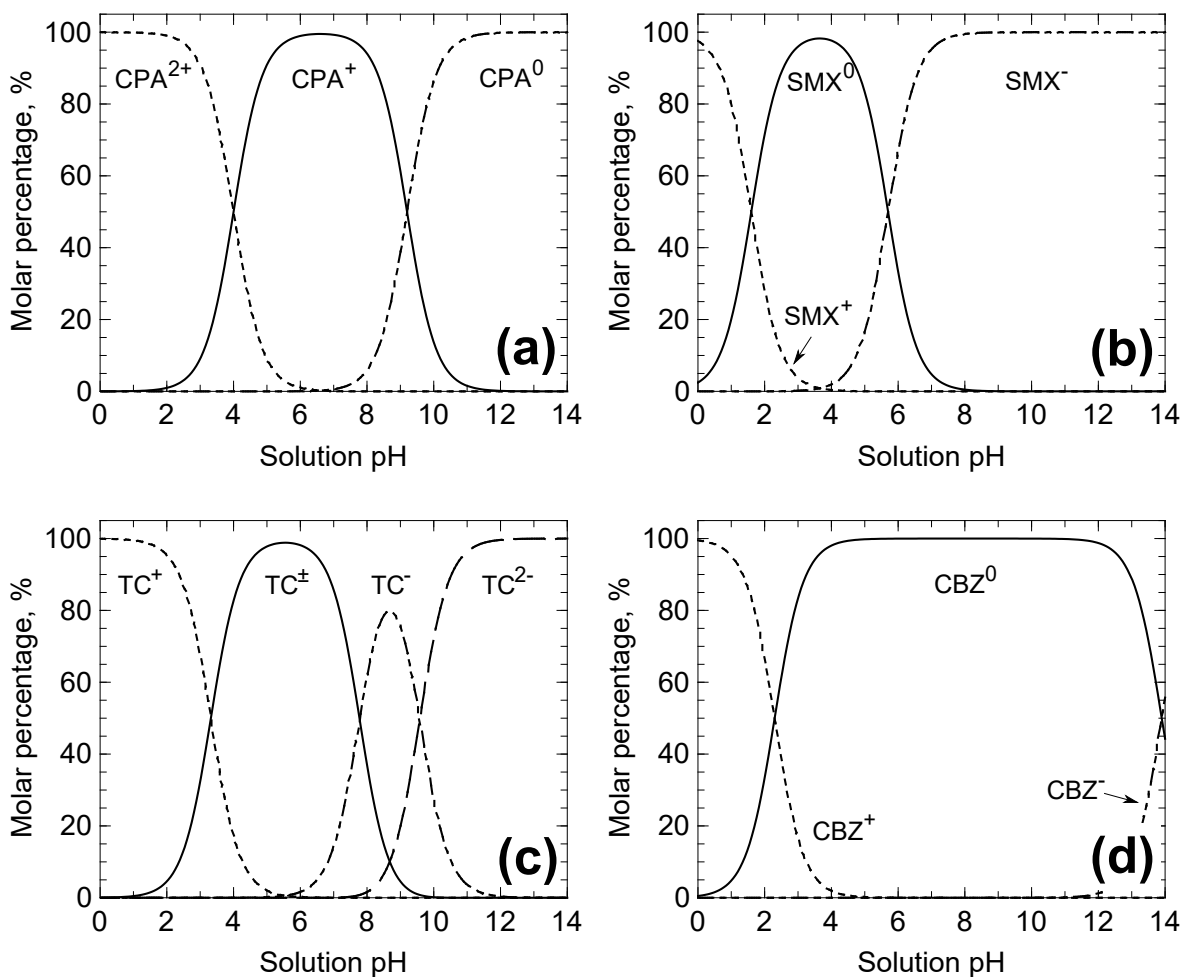
<sup>a</sup> Determined by Density Functional Theory (DFT) using 6-31G B3LYP method.

<sup>b</sup> Distribution coefficients calculated at pH = 7.

<sup>c</sup> Dissociation constants.

The pharmaceutical compounds possess ionizable functional groups that can coexist in solution in different ionic forms. The ionization of these groups and the molar percentage of each ionic form vary depending on the solution pH. Depending on the species that predominates under normal pH and temperature conditions,

pharmaceuticals can be classified as cationic, anionic, zwitterionic or neutral. As illustrated in Figure 8.1, at pH of 7, CPA is present as a cation, while SMX as an anion. On the other hand, TC predominantly exists as a zwitterion, whereas CBZ mainly exists as a neutral molecule in the aqueous solution.



**Figure 8.1.** Chemical species distribution diagrams of CPA (a), SMX (b), TC (c) and CBZ (d) at a total concentration of 0.5 mmol/L.

#### 8.2.4 Method for quantifying pharmaceutical compounds in aqueous solution

To quantify the concentrations of pharmaceutical compounds in aqueous solution, absorbance measurements were conducted using a Shimadzu UV-Vis spectrophotometer, model 2600. The specific wavelengths used were as follows: 261 nm for CPA, 257 nm for SMX, 357 nm for TC and 285 nm for CBZ. Calibration curves

employed for concentration determination were prepared within concentration ranges of 0.5 to 50 mg/L for CPA, 0.5 to 20 mg/L for SMX, 0.5 to 40 mg/L for TC and 0.5 to 20 mg/L for CBZ.

### **8.2.5 Estimation of distribution coefficients of pharmaceutical compounds**

The octanol-water partition coefficient, commonly abbreviated as  $K_{OW}$ , is a measure that assess the affinity of a non-ionizable organic compound for the aqueous and organic phases in a biphasic system composed of octanol and water at equilibrium. The logarithmic version of this coefficient is called  $\text{Log } K_{OW}$  and is calculated using the following equation:

$$\text{Log } K_{OW} = \text{Log} \left( \frac{[\text{Solute}]_{\text{octanol}}}{[\text{Solute}]_{\text{un-ionized water}}} \right) \quad (8.1)$$

where  $[\text{Solute}]_{\text{octanol}}$  is the concentration of the solute in the organic phase and  $[\text{Solute}]_{\text{un-ionized water}}$  is the concentration of the solute in the un-ionized aqueous phase.

According to this equation, an organic compound is considered hydrophobic when the  $\text{Log } K_{OW}$  value is greater than 1, while it is classified as hydrophilic when the  $\text{Log } K_{OW}$  value is less than 1.

It is important to note that pharmaceutical compounds often contain functional groups that can ionize depending on the solution pH. This ionization can significantly affect the partition coefficient, as the distribution of chemical species varies with pH. Since  $\text{Log } K_{OW}$  describes the hydrophobicity of the non-ionic form of a compound, the distribution coefficient ( $\text{Log } D$ ) is used to represent the hydrophobicity of any ionic form as a function of pH. The equation to calculate  $\text{Log } D$  values is as follows:

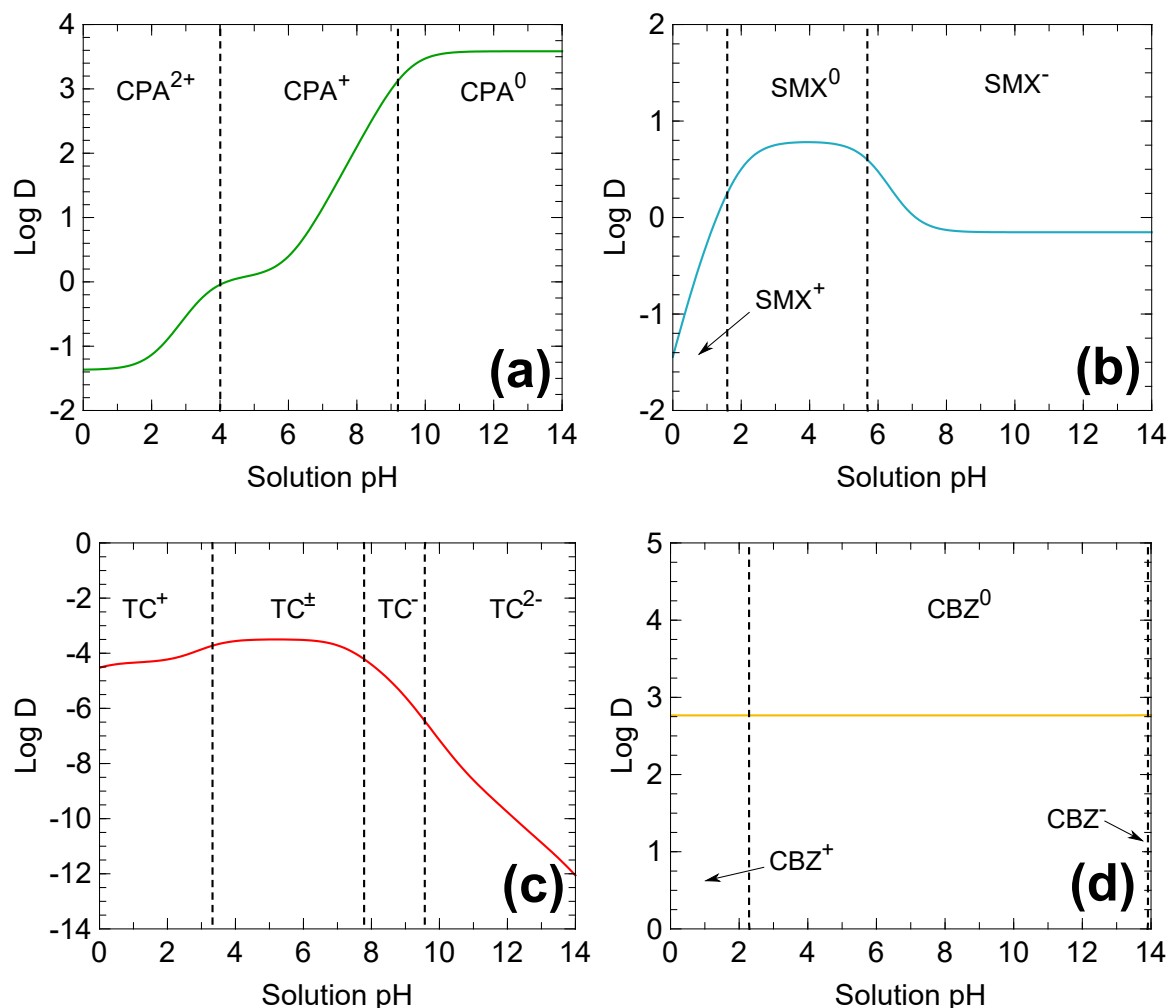
$$\text{Log } D = \text{Log} \left( \frac{[\text{Solute}]_{\text{octanol}}}{[\text{Solute}]_{\text{ionized water}} + [\text{Solute}]_{\text{un-ionized water}}} \right) \quad (8.2)$$

where  $[\text{Solute}]_{\text{ionized water}}$  is the concentration of the solute in an aqueous phase ionized at a certain pH.

Figure 8.2 presents diagrams illustrating the variation of distribution coefficients as a function of the solution pH, while maintaining a constant total concentration of 0.5 mmol/L. According to the figure, it can be noted that CPA exhibits hydrophilic affinity at



pH values below 7, while it becomes hydrophobic at pH values above 7. On the other hand, both SMX and TC show hydrophilic trend across the entire pH range analyzed, in contrast to CBZ, which exhibits hydrophobic behavior.



**Figure 8.2.** Variation of distribution coefficients of CPA (a), SMX (b), TC (c) and CBZ (d) as a function of solution pH at a total concentration of 0.5 mmol/L.

### 8.2.6 Technique for obtaining experimental adsorption equilibrium data

Experimental adsorption equilibrium data were collected using a batch adsorption system, its design is presented in Figure 4.2. The procedure for obtaining experimental adsorption equilibrium data follows a methodology similar to that described in Chapter 4, Section 4.2.5.

### **8.2.7 Procedure for measuring experimental adsorption kinetic data**

The concentration decay curves were obtained utilizing a stirred tank batch adsorber for suspended particles with recirculation, as illustrated in Figure 6.1. The methodology for measuring the experimental data of adsorption kinetics closely follows the procedure outlined in Chapter 6, Section 6.3.4.

## **8.3 Results and discussion**

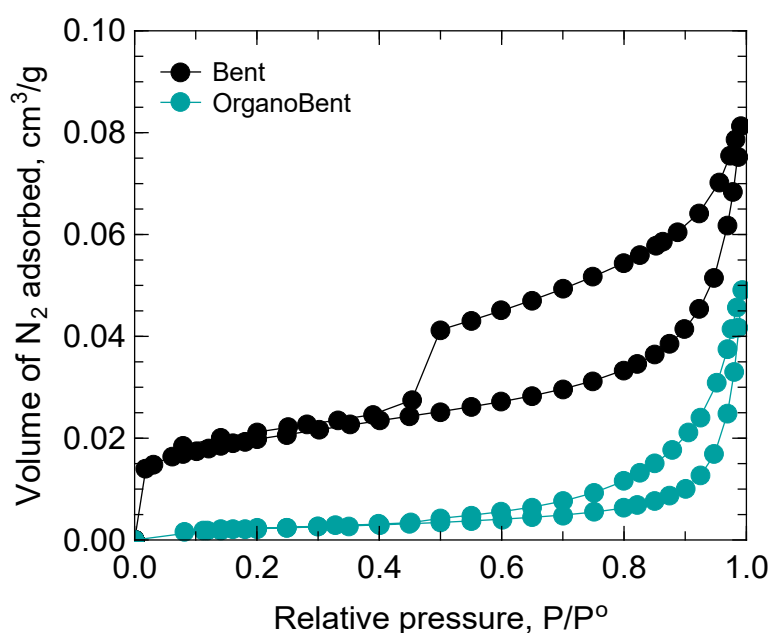
### **8.3.1 Textural, morphological and chemical characterization of bentonite and organobentonite**

The N<sub>2</sub> adsorption-desorption isotherms of Bent and OrganoBent are depicted in Figure 8.3. It is evident that both isotherms are classified as type IIb, characterized by the presence of an H3 hysteresis loop and the absence of a plateau at high  $P/P^0$  values. These characteristics result from the presence of slit-like mesopores, or in this case, disordered assemblies of clay lamellar particles. This disordered lamellar arrangement is the factor responsible for mesoporosity (Rouquerol et al., 1998). It can be noted from the figure that, following the modification of Bent with HDTMA, there is a notable decrease in the volume of N<sub>2</sub> adsorbed, along with a reduction in the amplitude of the hysteresis loop. These significant changes in the adsorption isotherms could be associated with the presence of HDTMA molecules coating the clay surface, thus obstructing its original mesoporosity.

The main textural properties of Bent and OrganoBent are listed in Table 8.2. Upon examining the table, it is notable that significant changes in textural properties occurred following organic modification.  $S_{\text{BET}}$  decreased by a factor of 9, while  $V_p$  decreased by approximately 1.4 times. Similarly, the values of  $S_{\text{meso}}$  and  $V_{\text{meso}}$  also experienced a substantial reduction, whereas  $D_p$  increased considerably. These findings suggest that HDTMA is adsorbed onto the clay surface, leading to the blocking of the original mesoporosity and the formation of new spaces with a larger average diameter.

Figure 8.4 provides a detailed view of the morphology of Bent and OrganoBent at different magnification levels in the highlighted areas in yellow and blue, respectively.

The images reveal that Bent exhibits a morphology characterized by disordered lamellar particles with sizes smaller than 30  $\mu\text{m}$ . Additionally, it is evident that following organic modification, OrganoBent displayed a drastic change in morphology. In this case, it is clearly noticeable that the mesopores originating from the disordered distribution of clay layers are blocked. This has led to the formation of aggregates on its surface and a significant increase in particle size, now reaching 86.7  $\mu\text{m}$ . This change in the morphology of OrganoBent clearly indicates a particle rearrangement and obstruction of clay mesoporosity.



**Figure 8.3.**  $\text{N}_2$  adsorption-desorption isotherms of Bent and OrganoBent at  $-196.15\text{ }^{\circ}\text{C}$ .

**Table 8.2.** Textural properties of Bent and OrganoBent.

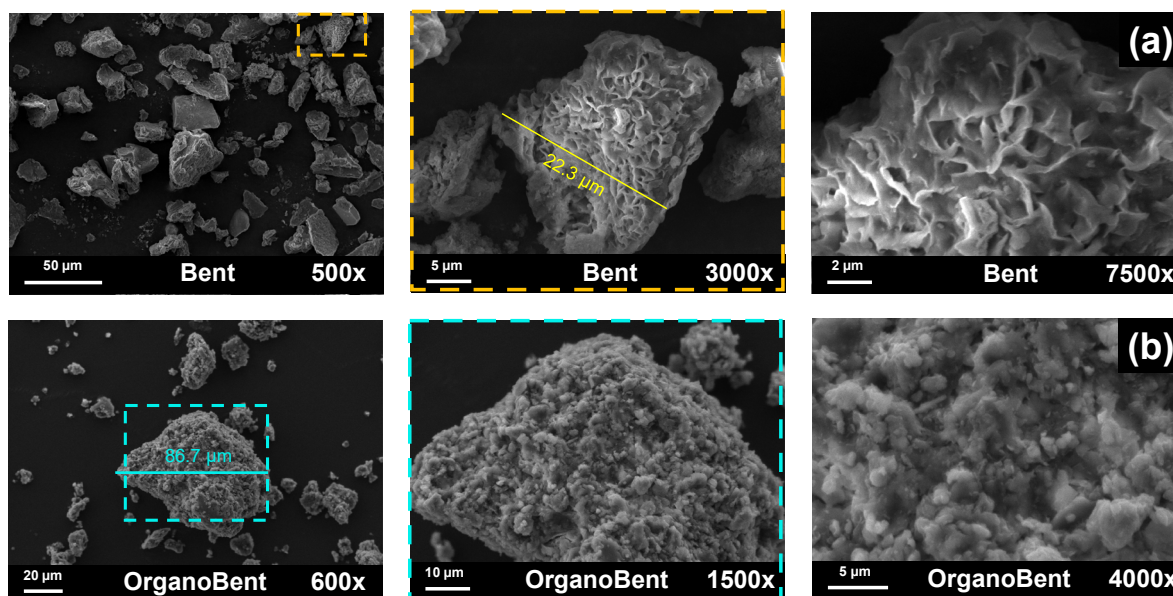
| Sample     | $S_{\text{BET}}^{\text{a}}$<br>( $\text{m}^2/\text{g}$ ) | $V_{\text{p}}^{\text{b}}$<br>( $\text{cm}^3/\text{g}$ ) | $D_{\text{p}}$<br>(nm) | $S_{\text{meso}}^{\text{c}}$<br>( $\text{m}^2/\text{g}$ ) | $V_{\text{meso}}^{\text{d}}$<br>( $\text{cm}^3/\text{g}$ ) |
|------------|----------------------------------------------------------|---------------------------------------------------------|------------------------|-----------------------------------------------------------|------------------------------------------------------------|
| Bent       | 45                                                       | 0.087                                                   | 7.8                    | 32                                                        | 0.075                                                      |
| OrganoBent | 5                                                        | 0.059                                                   | 45.0                   | 5                                                         | 0.037                                                      |

<sup>a</sup> Specific area determined by the BET method.

<sup>b</sup> Total pore volume evaluated by the BJH method.

<sup>c</sup> Mesopore area calculated by the t-plot method.

<sup>d</sup> Mesopore volume obtained by the BJH method.

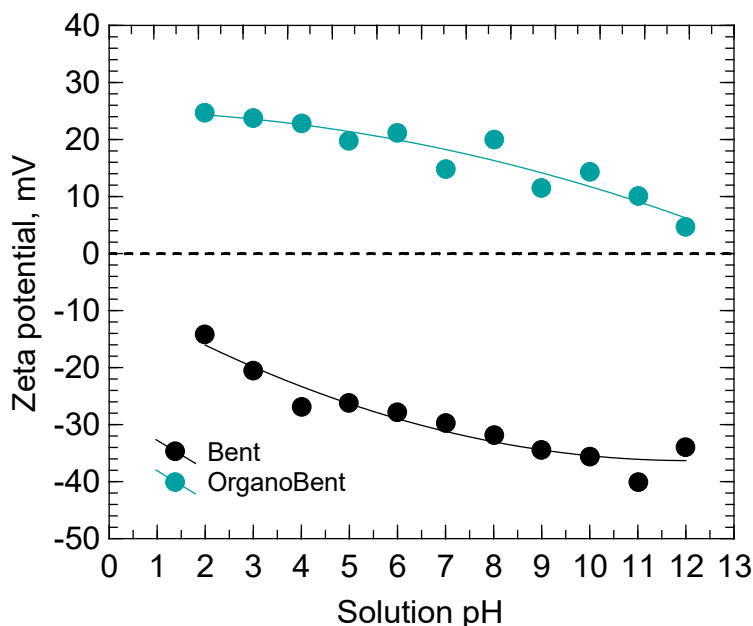


**Figure 8.4.** SEM images of Bent (a) and OrganoBent (b) at different magnifications.

The surface charge distribution of Bent and OrganoBent materials as a function of solution pH is depicted in Figure 8.5. In the case of Bent, a negative surface charge is observed, a common characteristic in clay materials. This negative charge originates from isomorphous substitutions occurring in octahedral and tetrahedral layers, where  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  cations are replaced by lower-charged atoms. This substitution leads to the accumulation of negative charges on the surface of Bent. On the other hand, the figure also illustrates that, following modification with HDTMA, OrganoBent exhibits a noticeable change in its surface charge. It now presents a positive surface charge across the entire pH range analyzed, decreasing as the solution pH increases. The changes in surface charge suggest that quaternary ammonium cations are adsorbed onto the clay surface, generating a positive surface charge. This indicates that HDTMA is adsorbed onto the cationic and negatively charged sites of the clay through electrostatic attraction mechanisms, creating anionic adsorption sites with positive charge. It is important to mention that the values of  $\text{pH}_{\text{IEP}}$  could not be estimated, but the figure indicates that is less than 2 for Bent and greater than 12 for OrganoBent.

Figure 8.6 displays the X-ray patterns for both the Bent and OrganoBent samples. In Chapter 4, Section 4.3.3, a detailed characterization was conducted,

allowing the identification of several crystalline phases in the Bent sample, including montmorillonite, feldspars, quartz and illite. This identification was carried out through meticulous comparison with data from the JCPDS 13-0135 crystallographic chart. Additionally, the basal spacing of the plane (001) was determined to be 1.50 nm. This value is associated with the presence of hydration water in the interlayer spaces of the structure.

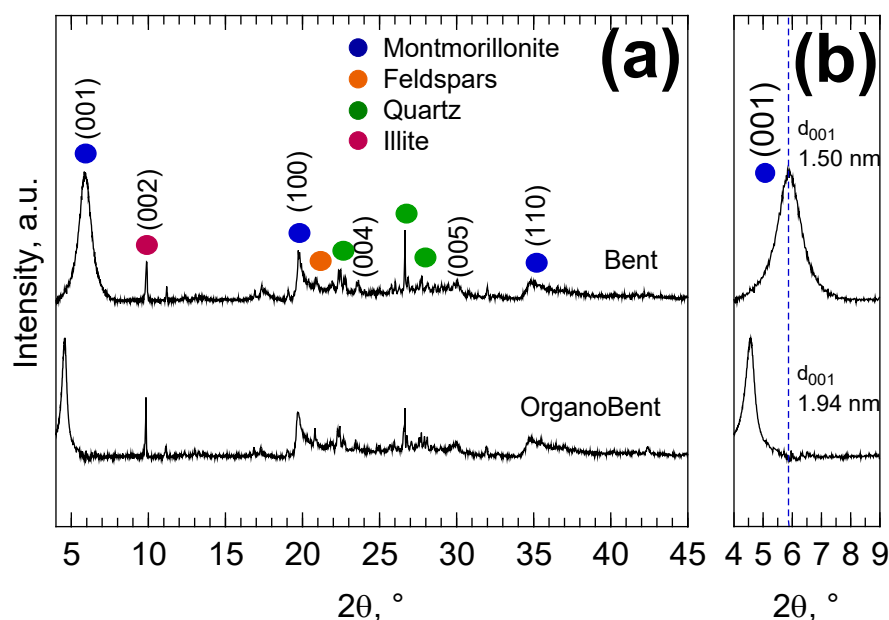


**Figure 8.5.** Surface charge distribution of Bent and OrganoBent.

Upon analyzing Figure 8.6 (a) regarding the OrganoBent sample, it is noted that the same crystalline phases identified in Bent are present. However, a significant change in the position of the reflection corresponding to the plane (001) is highlighted, which has shifted towards smaller angles. This displacement can be observed in greater detail in Figure 8.6 (b), which provides an enlarged view of the area corresponding to the plane (001).

The basal spacing of the plane (001), denoted as  $d_{001}$ , for OrganoBent was measured at 1.94 nm. According to Moore and Hower (1986), this implies an interlayer space of 0.98 nm. Density Functional Theory (DFT) calculations estimated the length of the HDTMA chain to be 2.3 nm, suggesting that HDTMA molecules intercalate into

the interlayer space of the clay in an inclined orientation relative to the clay layers. In a previous study by Lagaly et al. (2013), the variation of  $d_{001}$  was investigated based on the arrangement of the alkyl chains of the surfactant in the interlayer space. The authors concluded that when the value of  $d_{001}$  ranges between 1.77 and 2.0 nm, the surfactant chains are arranged in an inclined orientation, forming a double layer of molecules.

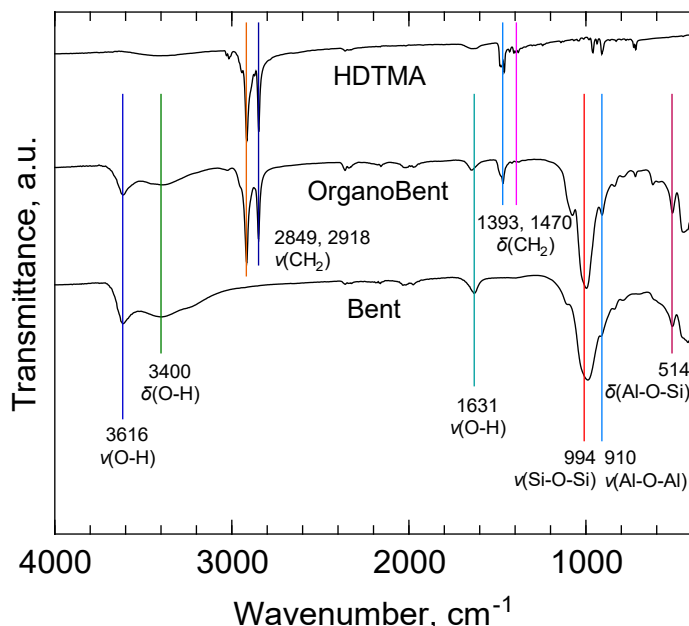


**Figure 8.6.** X-ray patterns of Bent and OrganoBent (a). Enlargement of the area corresponding to the reflection of the crystallographic plane (001) (b).

The obtained  $d_{001}$  value of 1.94 nm in the present study suggests that HDTMA molecules are adsorbed into the interlayer space of the clay, forming a bilayer of molecules. In this configuration, the first layer of molecules interacts with the negatively charged cationic sites on the clay surface through electrostatic attraction and cation exchange mechanisms, while the second layer of molecules interacts with the previously adsorbed monolayer through van der Waals interactions between the alkyl chains of the cationic surfactant.

The infrared spectra of the Bent, OrganoBent and HDTMA samples, spanning the wavenumber range between 400 and 4000  $\text{cm}^{-1}$ , are plotted in Figure 8.7. In

Chapter 4, Section 4.3.4, a detailed description of the assignment of each vibration band corresponding to the Bent sample is provided.



**Figure 8.7.** FT-IR spectra of Bent, OrganoBent and HDTMA.

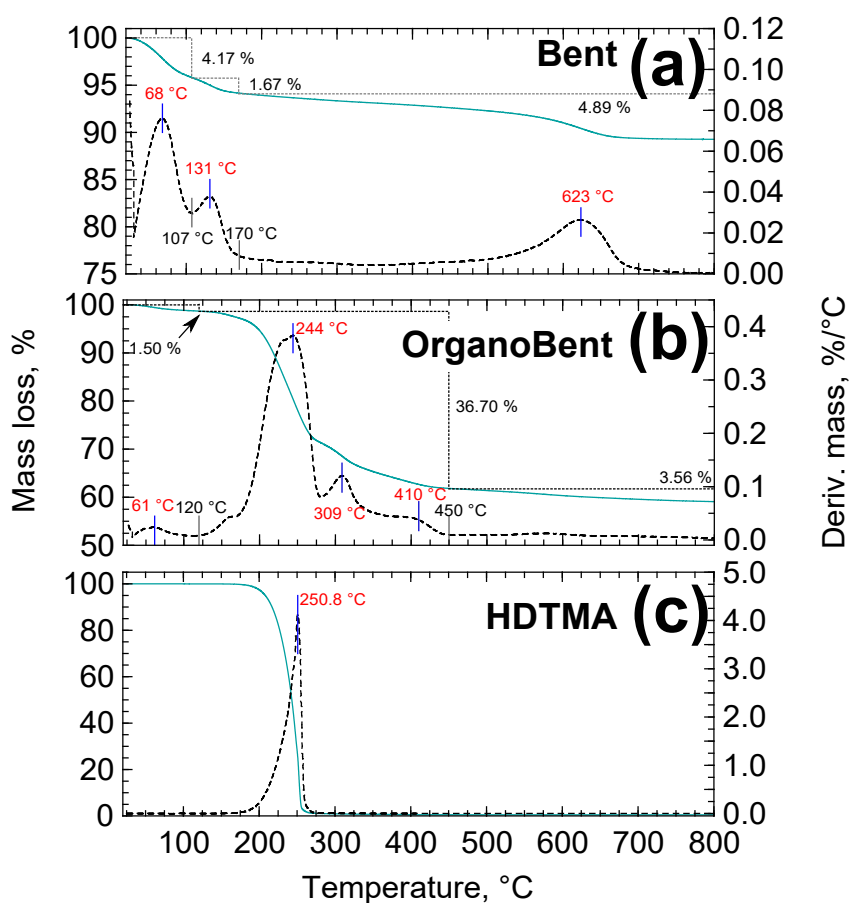
Additionally, the figure shows that the vibration bands identified in the Bent sample are also discernible in OrganoBent. However, notably intense bands at 2849 and 2918  $\text{cm}^{-1}$ , attributed to the asymmetric and symmetric vibrations of the methylene groups  $\nu(\text{CH}_2)$ , characteristic of HDTMA, are observed. Furthermore, bands between 1393 and 1470  $\text{cm}^{-1}$  are assigned to the bending vibrations  $\delta(\text{CH}_2)$  of the same groups. The presence of these vibrational bands in OrganoBent unequivocally indicates the modification of clay with HDTMA molecules.

The TGA/DTG curves of Bent, OrganoBent and HDTMA are depicted in Figure 8.8. Figure 8.8 (a) illustrates the thermal events that occurred in the Bent sample. A comprehensive analysis of the results of the different stages of mass loss of the Bent sample is detailed in Chapter 4, Section 4.3.5, where it was concluded that the total mass loss of Bent, in the temperature range of 25 to 800  $^{\circ}\text{C}$ , was 10.73 %.

The curves corresponding to the OrganoBent sample are presented in Figure 8.8 (b), revealing distinct thermal events not observed in the Bent sample. The initial

1.5 % mass loss, occurring near 61 °C, is attributed to the limited amount of water adsorbed on the surface of the organoclay. Subsequently, the second mass loss stage is due to the decomposition of the adsorbed surfactant, representing 36.7 % of the total mass loss.

Figure 8.8 (c) highlights the decomposition of HDTMA, occurring in a single stage between 200 and 260 °C. However, in OrganoBent, decomposition is observed in three consecutive stages. The main stage happened near to 244 °C, followed by continued decomposition of the surfactant until reaching 450 °C. This behavior is attributed to the sequential removal of surfactant initially adsorbed on the external surface, followed by surfactant adsorbed in the interlayer space.



**Figure 8.8.** TGA (blue line) and DTG (black dashed line) curves obtained for Bent (a), OrganoBent (b) and HDTMA (c).



### 8.3.2 Adsorption capacity towards cationic, anionic, zwitterionic and neutral pharmaceutical compounds

The adsorption isotherms of four pharmaceutical compounds: CPA, SMX, TC and CBZ on Bent and OrganoBent were obtained. These isotherms elucidate the effect of the chemical characteristics of the pharmaceutical compounds on the adsorption capacity of both materials.

To interpret the experimental data, three adsorption isotherm models were applied: Freundlich, Langmuir and Radke-Prausnitz, described by Equations (4.9-4.11). The results of these models, alongside the corresponding average percentage deviation, are summarized in Table 8.3. Parameter estimation was carried out through a nonlinear fitting of the experimental data, and the percentage deviation was computed using Equation (4.12).

**Table 8.3.** Adsorption isotherm parameters and average percentage deviation for the adsorption of CPA, SMX, TC and CBZ on Bent and OrganoBent at pH = 7 and T = 25 °C.

| Adsorbent  | Solute | Freundlich                                            |      |      | Langmuir                          |                               |      | Radke-Prausnitz              |                                           |         |      |
|------------|--------|-------------------------------------------------------|------|------|-----------------------------------|-------------------------------|------|------------------------------|-------------------------------------------|---------|------|
|            |        | K<br>( $\text{mg}^{1-1/n} \text{ L}^{1/n}/\text{g}$ ) | N    | %D   | $q_m$<br>( $\text{mg}/\text{g}$ ) | K<br>( $\text{L}/\text{mg}$ ) | %D   | a<br>( $\text{L}/\text{g}$ ) | b<br>( $\text{L}^\beta/\text{mg}^\beta$ ) | $\beta$ | %D   |
| Bent       | CPA    | 40.68                                                 | 3.40 | 23.4 | 159.18                            | 0.128                         | 5.1  | 21.50                        | 0.148                                     | 0.98    | 4.7  |
|            | SMX    | 0.042                                                 | 1.07 | 8.9  | 36.97                             | 0.001                         | 7.2  | 0.034                        | 0.024                                     | 0.47    | 8.1  |
|            | TC     | 22.83                                                 | 2.14 | 14.5 | 243.70                            | 0.034                         | 4.2  | 8.19                         | 0.034                                     | 1.00    | 4.2  |
|            | CBZ    | 0.066                                                 | 1.00 | 8.7  | 178.04                            | 0.0004                        | 9.6  | 0.0675                       | 0.0004                                    | 1.00    | 9.6  |
| OrganoBent | CPA    | 0.111                                                 | 1.04 | 12.7 | 107.93                            | 0.001                         | 12.3 | 0.1021                       | 0.001                                     | 1.00    | 12.3 |
|            | SMX    | 25.13                                                 | 2.95 | 26.1 | 126.69                            | 0.083                         | 11.9 | 10.55                        | 0.083                                     | 1.00    | 11.9 |
|            | TC     | 21.05                                                 | 2.17 | 21.0 | 245.10                            | 0.026                         | 4.2  | 6.40                         | 0.026                                     | 1.00    | 4.2  |
|            | CBZ    | 0.970                                                 | 1.15 | 17.8 | 205.63                            | 0.003                         | 11.9 | 0.7073                       | 0.003                                     | 1.00    | 11.9 |

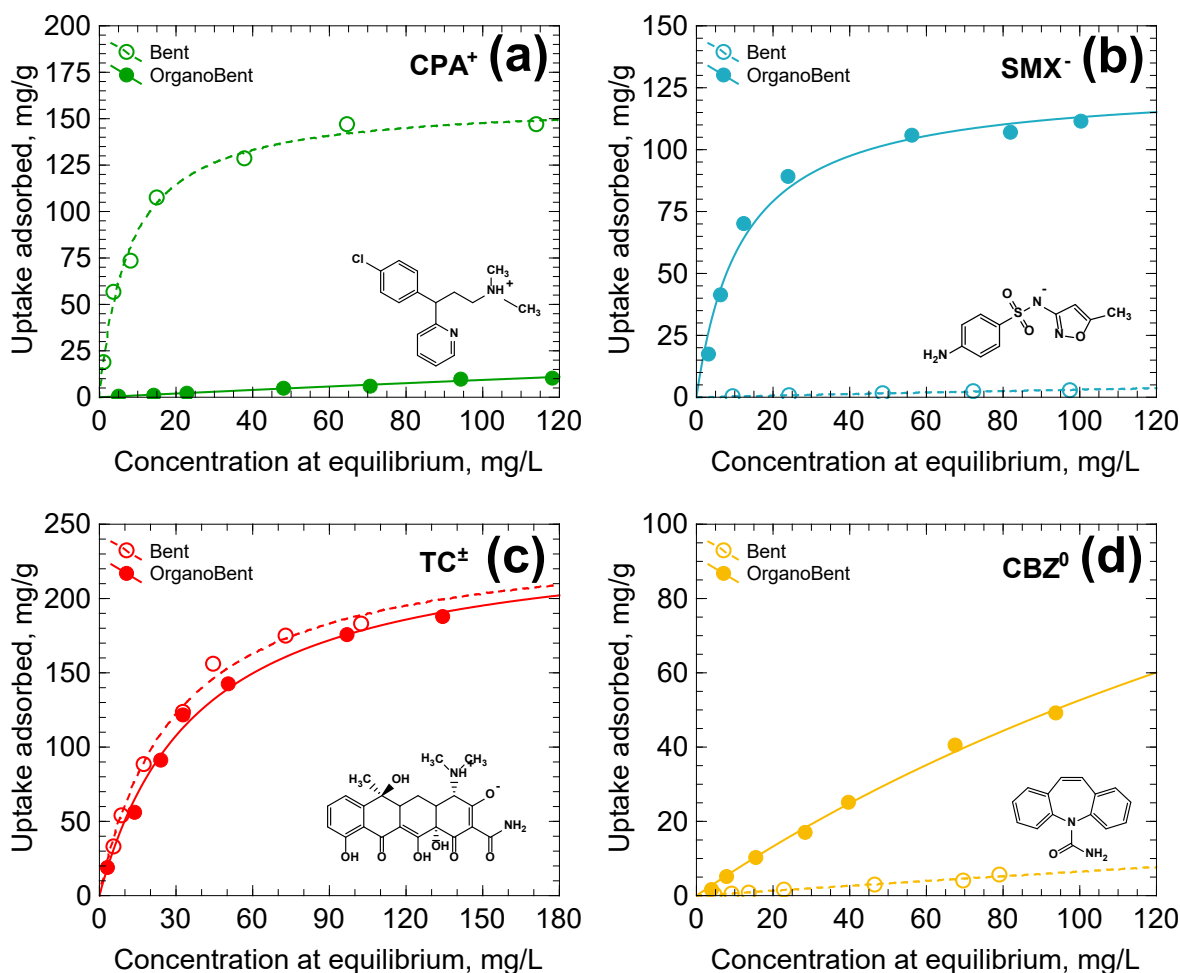
According to the table, the Langmuir isotherm model was chosen for interpreting the experimental data, as the %D values fell within the range of 4.2 to 12.3 %. In 7 out of the 8 cases analyzed, the Langmuir isotherm exhibited lower %D values compared to those obtained using the Freundlich isotherm. Additionally, the %D values calculated using the Radke-Prausnitz model closely resembled those obtained using the Langmuir

model. However, it is important to note that, in most cases, the value of  $\beta$  in the Radke-Prausnitz isotherm was equal to 1, implying a mathematical transformation of the Radke-Prausnitz isotherm into the Langmuir isotherm.

The adsorption isotherms of the cation  $\text{CPA}^+$ , anion  $\text{SMX}^-$ , zwitterion  $\text{TC}^\pm$  and neutral pharmaceutical  $\text{CBZ}^0$  on Bent and OrganoBent at  $\text{pH} = 7$  and  $T = 25^\circ\text{C}$  are depicted in Figure 8.9. In Figure 8.9 (a), it can be observed that Bent exhibits a significantly higher adsorption capacity for  $\text{CPA}^+$  compared to OrganoBent. For instance, at an equilibrium concentration of 100 mg/L, the uptakes adsorbed were 147.6 mg/g for Bent and only 9.8 mg/g for OrganoBent. The decrease in adsorption capacity for  $\text{CPA}^+$  in OrganoBent, reduced by 15.1 times due to organic modification, is surprising. Conversely, in Figure 8.9 (b), organic modification significantly increased the adsorption capacity towards  $\text{SMX}^-$ . At an equilibrium concentration of 100 mg/L, the uptakes adsorbed were 3.4 and 113.1 mg/g for Bent and OrganoBent, respectively, representing a 33.3-fold increase in adsorption capacity in OrganoBent. The adsorption isotherms of  $\text{TC}^\pm$  are presented in Figure 8.9 (c). Here, it is observed that the adsorption capacity of Bent towards  $\text{TC}^\pm$  is high, reaching 188.3 mg/g at an equilibrium concentration of 100 mg/L. After organic modification, the adsorption capacity remained mostly unchanged, reaching 177.0 mg/g at the same concentration. This indicates that organic modification did not significantly affect the adsorption capacity towards  $\text{TC}^\pm$ . Additionally, the adsorption isotherms of  $\text{CBZ}^0$  on Bent and OrganoBent are plotted in Figure 8.9 (d), where Bent exhibits a very low adsorption capacity that increases with organic modification. The adsorption capacities at an equilibrium concentration of 100 mg/L were 6.8 and 47.5 mg/g for Bent and OrganoBent, respectively, registering a 7.0-fold increase in adsorption capacity.

Figure 8.10 presents a comparison of the adsorption capacities of the pharmaceuticals  $\text{CPA}^+$ ,  $\text{SMX}^-$ ,  $\text{TC}^\pm$  and  $\text{CBZ}^0$  on Bent and OrganoBent at  $\text{pH} = 7$  and  $T = 25^\circ\text{C}$ , expressing the uptake adsorbed in units of mmol/kg. In Figure 8.10 (a), it is observed that Bent exhibits a high capacity to adsorb  $\text{CPA}^+$  and  $\text{TC}^\pm$  but low towards  $\text{SMX}^-$  and  $\text{CBZ}^0$ . At an equilibrium concentration of 0.4 mmol/L, the uptakes adsorbed of  $\text{CPA}^+$ ,  $\text{SMX}^-$ ,  $\text{TC}^\pm$  and  $\text{CBZ}^0$  were 540.8, 12.3, 469.7 and 26.1 mmol/kg, respectively.

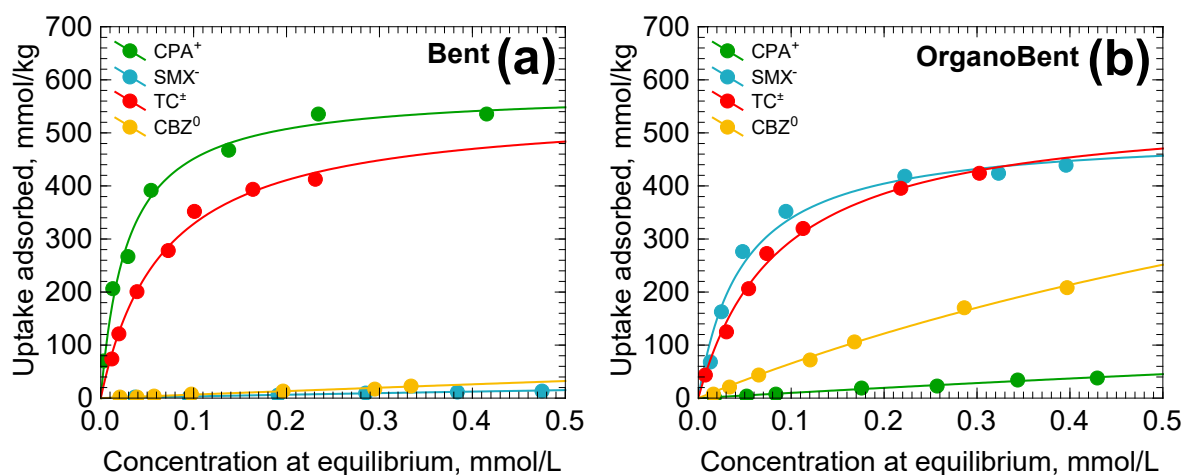
These results suggest that electrostatic interactions play a crucial role in adsorption.  $\text{CPA}^+$  and  $\text{TC}^\pm$  can electrostatically interact with the negative surface of Bent, while in the case of  $\text{SMX}^-$ , there is electrostatic repulsion, and  $\text{CBZ}^0$  does not exhibit electrostatic attraction to the surface of Bent.



**Figure 8.9.** Adsorption isotherms of  $\text{CPA}^+$  (a),  $\text{SMX}^-$  (b),  $\text{TC}^\pm$  (c) and  $\text{CBZ}^0$  (d) on Bent and OrganoBent at pH = 7, I = 0.01 N and T = 25 °C. The lines represent the Langmuir adsorption isotherm.

On the other hand, Figure 8.10 (b) shows that OrganoBent displays high adsorption capacities towards  $\text{TC}^\pm$ ,  $\text{SMX}^-$  and  $\text{CBZ}^0$ , but lacks adsorption capacity towards  $\text{CPA}^+$ . The uptakes adsorbed, at an equilibrium concentration of 0.4 mmol/L, were 37.0, 447.2, 453.8 and 213.5 mmol/kg for  $\text{CPA}^+$ ,  $\text{SMX}^-$ ,  $\text{TC}^\pm$  and  $\text{CBZ}^0$ ,

respectively, and the adsorption capacity decreased in the following order:  $TC^{\pm} \approx SMX^{-} > CBZ^0 > CPA^{+}$ . These results suggest that the decrease in the adsorption capacity of  $CPA^{+}$  is due to electrostatic repulsions with the positive surface of OrganoBent. Additionally, the adsorption of  $SMX^{-}$  and  $TC^{\pm}$  is driven by electrostatic attraction between the negatively charged pharmaceuticals and the positively charged surface of OrganoBent. In addition to these electrostatic interactions, the organophilic interactions and the hydrophobic partitioning of  $SMX^{-}$  and  $TC^{\pm}$  between the solution and the organic phase of OrganoBent may contribute to the adsorption capacity. The results of  $CBZ^0$  adsorption on OrganoBent cannot be explained by electrostatic interactions due to its neutral charge. In this case, adsorption on OrganoBent may be associated solely with the hydrophobic and organophilic nature of OrganoBent, as well as the hydrophobicity of CBZ. According to Table 8.1, the Log D value of CBZ is 2.77, indicating that is highly hydrophobic.



**Figure 8.10.** Comparison of the adsorption isotherms of  $CPA^{+}$ ,  $SMX^{-}$ ,  $TC^{\pm}$  and  $CBZ^0$  on Bent (a) and OrganoBent (b) at pH = 7, I = 0.01 N and T = 25 °C. The lines represent the Langmuir adsorption isotherm.

These results lead to the conclusion that the charge and surface nature of Bent and OrganoBent, as well as the ionic charge and hydrophobicity of the pharmaceutical compound, play a fundamental role in the adsorption of pharmaceutical compounds. Furthermore, it is observed that Bent exhibits a high affinity towards cationic and

zwitterionic pharmaceuticals, whereas OrganoBent does so for anionic, zwitterionic and neutral pharmaceutical compounds.

### 8.3.3 Effect of the surface charge of bentonite and organobentonite on adsorption capacity

The impact of the surface charge of Bent and OrganoBent on adsorption capacity was evaluated by examining variations in surface charge as a function of the uptake of adsorbed compound. The studied adsorption systems include CPA<sup>+</sup> and TC<sup>±</sup> on Bent, and SMX<sup>-</sup> and TC<sup>±</sup> on OrganoBent. CBZ<sup>0</sup> was excluded from this analysis due to its neutral charge. Changes in surface charge were calculated using the Zeta potential gradient,  $\Delta(ZP)$ , with the following equations:

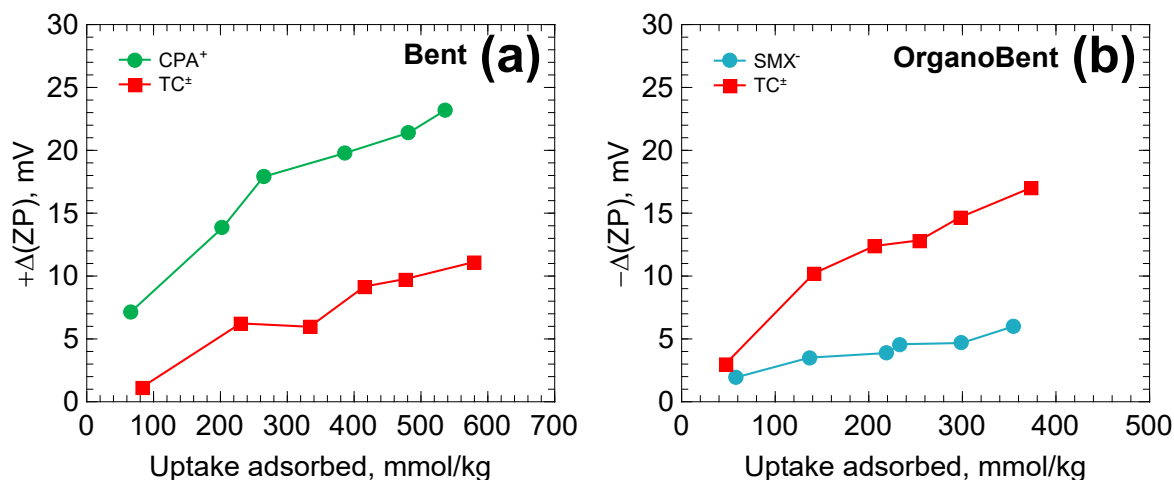
$$\Delta(ZP) = (ZP)_{\text{Bent} + \text{CFA/TC}} - (ZP)_{\text{Bent}} \quad (8.3)$$

$$\Delta(ZP) = (ZP)_{\text{OrganoBent} + \text{SMX/TC}} - (ZP)_{\text{OrganoBent}} \quad (8.4)$$

where  $(ZP)_{\text{Bent} + \text{CFA/TC}}$  represents the Zeta potential of Bent at an uptake adsorbed of CPA<sup>+</sup> or TC<sup>±</sup>, mV;  $(ZP)_{\text{OrganoBent} + \text{SMX/TC}}$  corresponds to the Zeta potential of OrganoBent with SMX<sup>-</sup> or TC<sup>±</sup> adsorbed, mV;  $(ZP)_{\text{Bent}}$  and  $(ZP)_{\text{OrganoBent}}$  are the Zeta potentials of Bent and OrganoBent, mV.

The variations in Zeta potential concerning the uptake adsorbed is presented in Figure 8.11. It can be observed that  $\Delta(ZP)$  increased with the uptake of drug adsorbed for all cases. A positive value of  $\Delta(ZP)$  in the adsorption of CPA<sup>+</sup> and TC<sup>±</sup> on Bent (Figure 8.11 (a)) indicates that the negative surface charge of Bent became less negative. Conversely, the negative  $\Delta(ZP)$  value for the adsorption of SMX<sup>-</sup> and TC<sup>±</sup> on OrganoBent (Figure 8.11 (b)) suggests that the positive surface charge of OrganoBent became less positive. These findings imply that CPA<sup>+</sup> and TC<sup>±</sup> were adsorbed onto the cationic sites of Bent, neutralizing its negative surface charge. In contrast, SMX<sup>-</sup> and TC<sup>±</sup> were adsorbed onto the anionic sites of OrganoBent, counteracting its positive surface charge. These observations highlight the significance of electrostatic attractions in the adsorption of CPA<sup>+</sup> and TC<sup>±</sup> on Bent, as well as SMX<sup>-</sup> and TC<sup>±</sup> on OrganoBent. Thiebault and Boussafir (2019) studied the adsorption of psychoactive

drugs on Na-montmorillonite and reported that electrostatic attractions are involved in the adsorption of cationic codeine on the sodic clay. Similarly, in another study, the adsorption of amoxicillin on an organomontmorillonite modified with the amino acid L-methionine was examined, with the authors concluding that electrostatic forces favored the ability of the organoclay to adsorb amoxicillin in its anionic form (Imanipoor et al., 2021).



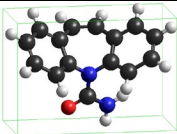
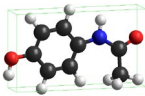
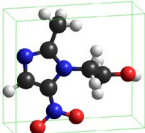
**Figure 8.11.** Variation of the Zeta potential for Bent (a) and OrganoBent (b) as a function of the uptake of CPA<sup>+</sup>, SMX<sup>-</sup> and TC<sup>+</sup> adsorbed.

### 8.3.4 Effect of the hydrophobicity of the pharmaceutical compound on adsorption capacity

The influence of solute hydrophobicity on adsorption mechanisms on OrganoBent was conducted as follows. Adsorption isotherms were generated on OrganoBent for a selection of neutral drugs with varying Log D values. This approach aimed to isolate the impact of solute hydrophobicity on the adsorption capacity of OrganoBent, thereby excluding the effects of electrostatic attractions in the adsorption process. The chosen neutral pharmaceuticals for this study included carbamazepine (CBZ), acetaminophen (ACE) and metronidazole (MNZ), with their key physicochemical properties outlined in Table 8.4. These drugs remain in their neutral state at pH = 7 and are denoted as CBZ<sup>0</sup>, ACE<sup>0</sup> and MNZ<sup>0</sup>. Additionally, adsorption isotherms of chlorphenamine (CPA) and trimethoprim (TMP) on OrganoBent were

incorporated, assessed at pH = 11, where they are also neutral, represented as CPA<sup>0</sup> and TMP<sup>0</sup>. Figure 8.12 illustrates the adsorption isotherms of CBZ<sup>0</sup>, ACE<sup>0</sup>, MNZ<sup>0</sup>, CPA<sup>0</sup> and TMP<sup>0</sup> on OrganoBent, alongside the adsorption isotherms of SMX<sup>-</sup> and TC<sup>±</sup>. Furthermore, the fitted parameters and average percentage deviation of the adsorption isotherms are tabulated in Table 8.5. The Langmuir isotherm model was deemed the most suitable for interpreting the experimental data of adsorption equilibrium.

**Table 8.4.** Physicochemical properties of CBZ<sup>0</sup>, ACE<sup>0</sup> and MNZ<sup>0</sup>.

| Pharmaceuticals                                       | Molecular structure <sup>a</sup>                                                    | Molecular size <sup>a</sup><br>(nm) | Log D <sup>b</sup> | pK <sub>a</sub> <sup>c</sup> |
|-------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------|--------------------|------------------------------|
| Carbamazepine<br>(CBZ <sup>0</sup> )<br>M.W. = 236.27 |    | X = 0.90<br>Y = 0.63<br>Z = 0.48    | 2.77               | 2.30, 13.90                  |
| Acetaminophen<br>(ACE <sup>0</sup> )<br>M.W. = 151.16 |   | X = 0.78<br>Y = 0.46<br>Z = 0.18    | 0.91               | 9.38                         |
| Metronidazole<br>(MNZ <sup>0</sup> )<br>M.W. = 171.15 |  | X = 0.72<br>Y = 0.64<br>Z = 0.29    | -0.46              | 2.58, 14.44                  |

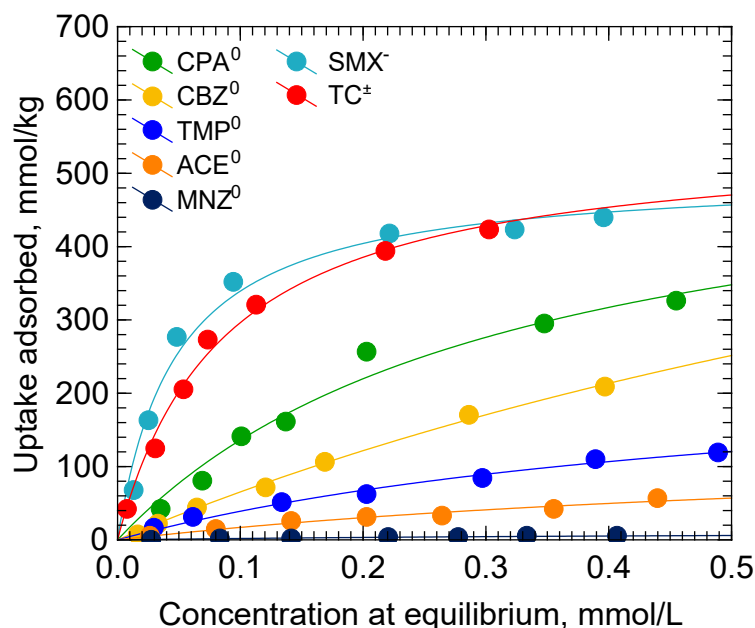
<sup>a</sup> Determined by Density Functional Theory (DFT) using 6-31G B3LYP method.

<sup>b</sup> Distribution coefficients calculated at pH = 7.

<sup>c</sup> Dissociation constants.

The figure illustrates that OrganoBent displayed enhanced adsorption capacities for SMX<sup>-</sup> and TC<sup>±</sup> due to the involvement of electrostatic attractions in the adsorption mechanism. Regarding neutral pharmaceuticals, OrganoBent demonstrated superior adsorption capacity for CPA<sup>0</sup> and inferior capacity for MNZ<sup>0</sup>, showing a decreasing adsorption trend as follows: CPA<sup>0</sup> > CBZ<sup>0</sup> > TMP<sup>0</sup> > ACE<sup>0</sup> > MNZ<sup>0</sup>. Calculated Log D values for CBZ<sup>0</sup>, ACE<sup>0</sup> and MNZ<sup>0</sup> at pH = 7 were 2.77, 0.91 and -0.46, respectively. Conversely, Log D values for CPA and TMP evaluated at pH = 11 were 3.57 and 1.28, respectively. These Log D values indicate that CPA is the most hydrophobic drug, while

MNZ is the least hydrophobic. Notably, the Log D values of the drugs followed the same order as the decrease in adsorption capacity.



**Figure 8.12.** Adsorption isotherms of CPA, CBZ, TMP, ACE, MNZ, SMX and TC on OrganoBent at T = 25 °C. Adsorption isotherms of CBZ, ACE, MNZ, SMX and TC were evaluated at pH = 7. Adsorption isotherms of CPA and TMP were obtained at pH = 11. The lines represent the Langmuir adsorption isotherm.

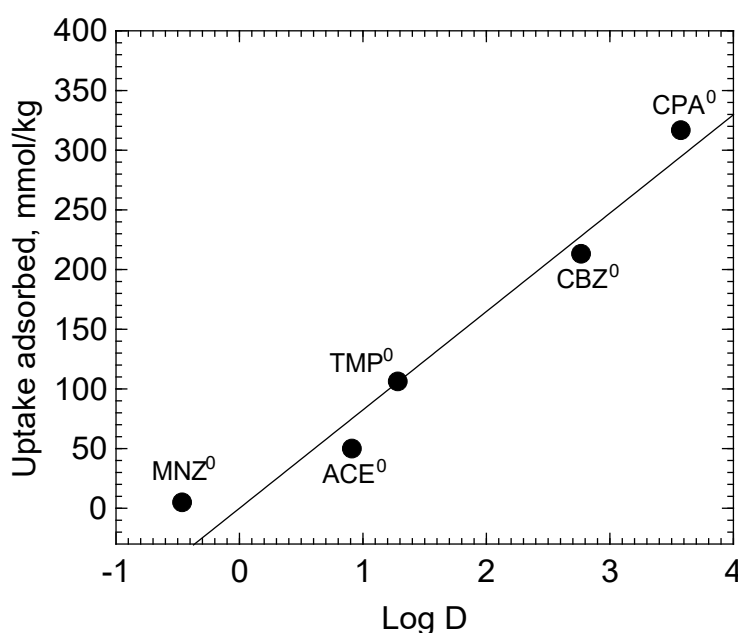
**Table 8.5.** Adsorption isotherm parameters and average percentage deviation for the adsorption of CBZ<sup>0</sup>, ACE<sup>0</sup>, MNZ<sup>0</sup>, CPA<sup>0</sup> and TMP<sup>0</sup> on OrganoBent.

| Solute           | pH | Freundlich                                       |      |      | Langmuir                   |               |      | Radke-Prausnitz |                                           |      |      |
|------------------|----|--------------------------------------------------|------|------|----------------------------|---------------|------|-----------------|-------------------------------------------|------|------|
|                  |    | K<br>(mmol <sup>1-1/n</sup> L <sup>1/n</sup> /g) | n    | %D   | q <sub>m</sub><br>(mmol/g) | K<br>(L/mmol) | %D   | a<br>(L/g)      | b<br>(L <sup>β</sup> /mmol <sup>β</sup> ) | β    | %D   |
| CBZ <sup>0</sup> | 7  | 481.88                                           | 1.15 | 17.8 | 870.30                     | 0.813         | 11.9 | 707.34          | 0.813                                     | 1.00 | 11.9 |
| ACE <sup>0</sup> | 7  | 98.85                                            | 1.34 | 8.2  | 137.62                     | 1.415         | 7.9  | 349.99          | 2.734                                     | 0.45 | 6.7  |
| MNZ <sup>0</sup> | 7  | 10.35                                            | 1.40 | 12.3 | 12.63                      | 1.801         | 12.1 | 29.00           | 2.173                                     | 0.67 | 10.2 |
| CPA <sup>0</sup> | 11 | 568.63                                           | 1.59 | 17.4 | 569.14                     | 3.145         | 11.9 | 1790.21         | 3.145                                     | 1.00 | 11.9 |
| TMP <sup>0</sup> | 11 | 199.08                                           | 1.46 | 4.5  | 252.80                     | 1.828         | 9.4  | 991.55          | 4.195                                     | 0.47 | 5.0  |

Figure 8.13 depicts the influence of Log D on the uptake of neutrally charged compounds adsorbed. Experimental data were obtained at T = 25 °C and an equilibrium



concentration of 0.4 mmol/L. The figure demonstrates that the adsorption capacity of OrganoBent linearly correlates with the distribution coefficient of the pharmaceuticals, reflecting the degree of hydrophobicity of the medications. Furthermore, it was observed that the adsorption capacity of OrganoBent increased proportionally with higher Log D values. These findings highlight the contribution hydrophobic and organophilic properties of OrganoBent, coupled with the degree of hydrophobicity of the pharmaceuticals, to the adsorption process via hydrophobic partitioning between the solution and the alkyl chains of the surfactant.



**Figure 8.13.** Effect of the distribution coefficient on the uptake of neutrally charged drugs adsorbed onto OrganoBent at  $T = 25\text{ }^{\circ}\text{C}$  and  $C_e = 0.4\text{ mmol/L}$ . CBZ<sup>0</sup>, ACE<sup>0</sup> and MNZ<sup>0</sup> experiments were evaluated at pH = 7. CPA<sup>0</sup> and TMP<sup>0</sup> experiments were conducted at pH = 11. The line represents the linear fit of the data.

### 8.3.5 Effect of solution pH, ionic strength and temperature on the capacity of organobentonite to adsorb SMX

The study investigated the impact of solution pH, ionic strength and solution temperature on the adsorption behavior of SMX on OrganoBent, with results presented in Figure 8.14. Additionally, Table 8.6 lists the parameters derived from the adsorption

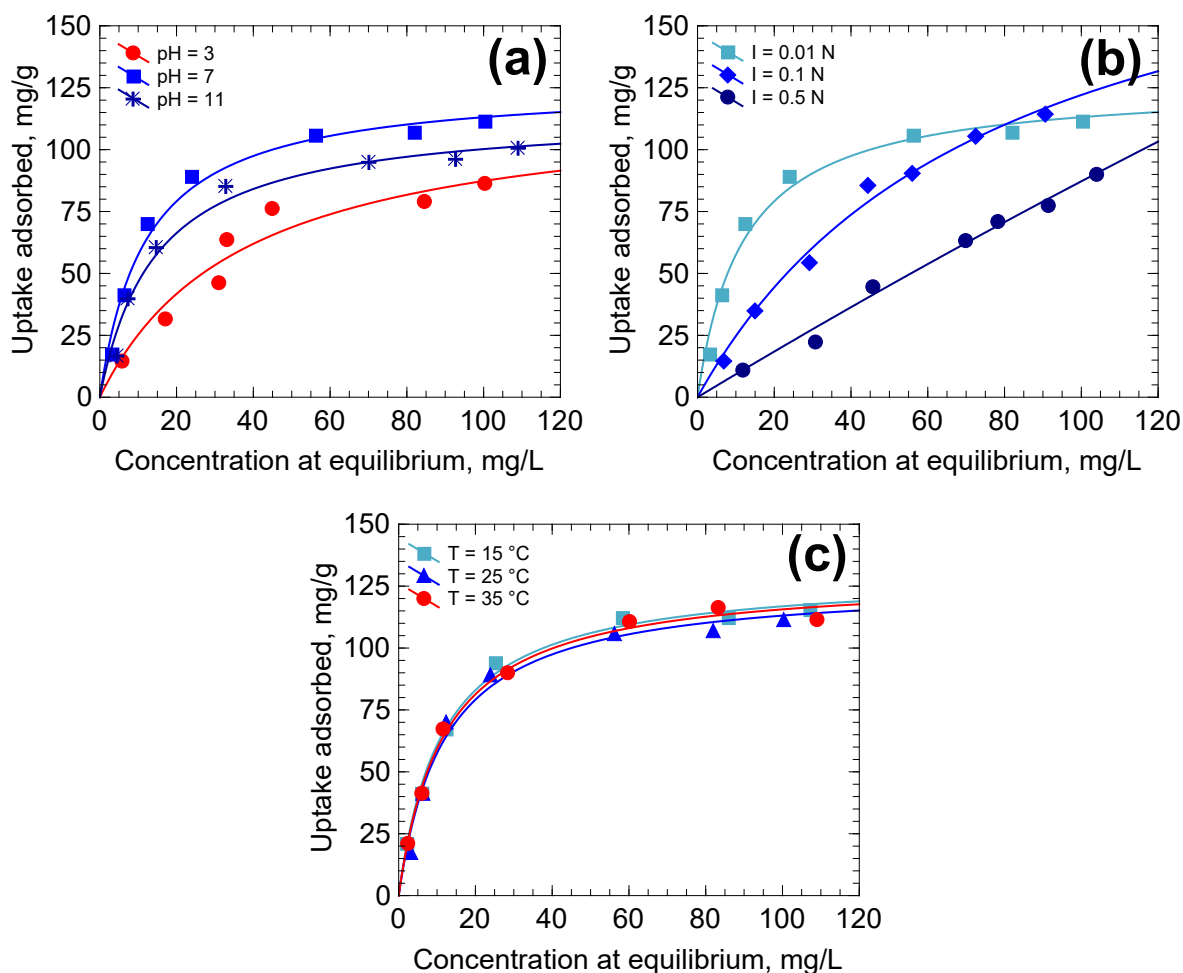
isotherms along with the average percentage deviation. In Figure 8.14 (a), the influence of solution pH on the capacity of OrganoBent to adsorb SMX at  $T = 25\text{ }^{\circ}\text{C}$  and pH values of 3, 7, and 11 is illustrated. The findings highlight the substantial effect of solution pH on the adsorption capacity. Maximum adsorption occurred at  $\text{pH} = 7$ , reaching  $111.4\text{ mg/g}$ . At pH values of 3 and 11, the maximum adsorption capacities were  $86.2$  and  $100.4\text{ mg/g}$ , respectively. This trend suggests that the adsorption capacity of OrganoBent for SMX increases as pH rises from 3 to 7, but declines as pH increases from 7 to 11. This behavior is attributed to the varying chemical species of SMX in solution and the surface charge characteristics of OrganoBent. At  $\text{pH} = 3$ , the prevalence of the neutral species  $\text{SMX}^0$  results in low adsorption capacity due to the absence of electrostatic interactions. Conversely, at  $\text{pH} = 7$ , the presence of the negative species  $\text{SMX}^-$  leads to a significant adsorption capacity owing to electrostatic attraction with the positively charged surface of OrganoBent. However, at  $\text{pH} = 11$ , despite the presence of  $\text{SMX}^-$ , the adsorption capacity slightly decreases due to the  $\text{pH}_{\text{IEP}}$  value of OrganoBent, which limits electrostatic interactions.

**Table 8.6.** Adsorption isotherm parameters and average percentage deviation for the adsorption of SMX on OrganoBent.

| pH | I<br>(N) | T<br>( $^{\circ}\text{C}$ ) | Freundlich                                           |      |      | Langmuir                   |                        |      | Radke-Prausnitz       |                                               |         |      |
|----|----------|-----------------------------|------------------------------------------------------|------|------|----------------------------|------------------------|------|-----------------------|-----------------------------------------------|---------|------|
|    |          |                             | K<br>( $\text{mg}^{1-1/n}\text{ L}^{1/n}/\text{g}$ ) | n    | %D   | $q_m$<br>( $\text{mg/g}$ ) | K<br>( $\text{L/mg}$ ) | %D   | a<br>( $\text{L/g}$ ) | b<br>( $\text{L}^{\beta}/\text{mg}^{\beta}$ ) | $\beta$ | %D   |
| 3  | 0.01     | 25                          | 9.75                                                 | 2.07 | 19.1 | 120.12                     | 0.0266                 | 11.1 | 3.200                 | 0.0266                                        | 1.00    | 11.1 |
| 7  | 0.01     | 25                          | 25.13                                                | 2.95 | 26.1 | 126.69                     | 0.0833                 | 11.9 | 10.549                | 0.0833                                        | 1.00    | 11.9 |
| 11 | 0.01     | 25                          | 20.54                                                | 2.85 | 22.2 | 114.90                     | 0.0682                 | 11.0 | 7.842                 | 0.0682                                        | 1.00    | 11.0 |
| 7  | 0.1      | 25                          | 6.17                                                 | 1.52 | 11.3 | 216.97                     | 0.0129                 | 5.3  | 2.791                 | 0.0129                                        | 1.00    | 5.3  |
| 7  | 0.5      | 25                          | 1.01                                                 | 1.03 | 6.2  | 1181.78                    | 0.0008                 | 5.9  | 0.936                 | 0.0008                                        | 1.00    | 5.9  |
| 7  | 0.01     | 15                          | 27.34                                                | 3.07 | 18.3 | 130.13                     | 0.0881                 | 3.6  | 11.459                | 0.0881                                        | 1.00    | 3.6  |
| 7  | 0.01     | 35                          | 26.10                                                | 3.00 | 18.3 | 129.25                     | 0.0848                 | 4.0  | 10.965                | 0.0848                                        | 1.00    | 4.0  |

The Figure 8.14 (b) illustrates the effect of solution ionic strength on the capacity of OrganoBent to adsorb SMX at  $T = 25\text{ }^{\circ}\text{C}$ . The isotherms reveal a decline in adsorption capacity with increasing solution ionic strength. For instance, at an equilibrium concentration of  $50\text{ mg/L}$ , the adsorption capacity decreased by 2.3 times

as the solution ionic strength rose from 0.01 to 0.5 N. This decline arises from the competition between  $\text{Cl}^-$  ions and  $\text{SMX}^-$  for the anionic sites on the positively charged surface of OrganoBent, highlighting the importance of electrostatic interactions in SMX adsorption mechanisms on OrganoBent.



**Figure 8.14.** Effect of solution pH (a), ionic strength (b) and temperature (c) on the adsorption isotherms of SMX on OrganoBent. The lines represent the Langmuir adsorption isotherm.

Concerning the impact of solution temperature, an investigation was conducted at pH = 7 and temperatures of 15, 25 and 35 °C, as depicted in Figure 8.14 (c). The findings indicate that solution temperature has no discernible effect on the adsorption capacity, as the isotherms overlap. The maximum adsorption capacities remain very

similar, around 112 mg/g, suggesting that the influence of solution temperature on the adsorption capacity for SMX is negligible.

### 8.3.6 Adsorption rate of SMX on organobentonite

The experimental data of the concentration decay curves of SMX during adsorption on OrganoBent were interpreted using the External Mass Transport Model (EMTM), Equations (6.1-6.4), and Pore Volume Diffusion Model (PVDM), Equations (6.5-6.10). It is important to note that the latter model assumes  $D_{e,s} = 0$ . The experimental conditions are listed in Table 8.7.

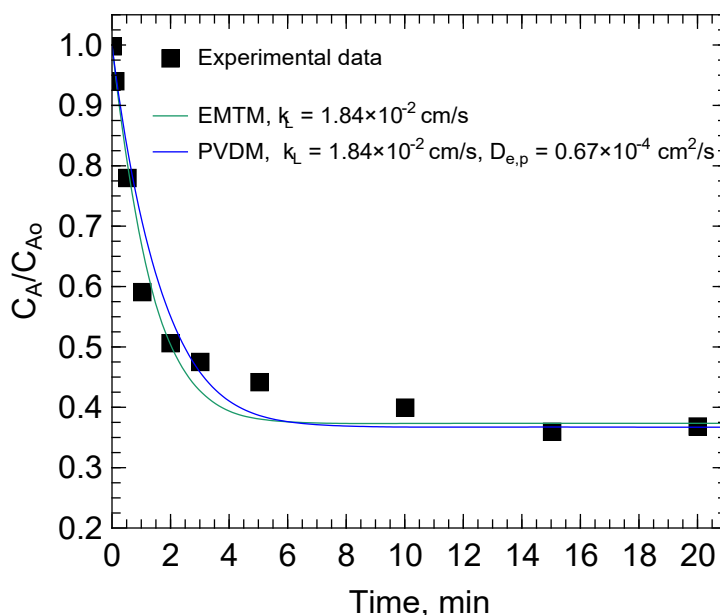
**Table 8.7.** Mass transport parameters for the adsorption of SMX on OrganoBent at pH = 7, T = 25 °C, m = 0.1 g, R = 0.0027 cm, V = 0.2 L and RPM = 450.

| Exp. No. | $C_{A0}$ (mg/L) | $C_{Ae}$ (mg/L) | $q_e$ (mg/g) | EMTM model               |     | PVDM model                                 |          |     |
|----------|-----------------|-----------------|--------------|--------------------------|-----|--------------------------------------------|----------|-----|
|          |                 |                 |              | $k_L \times 10^2$ (cm/s) | %Dd | $D_{e,p} \times 10^4$ (cm <sup>2</sup> /s) | $\tau_p$ | %Dd |
| 1        | 26.73           | 7.32            | 38.54        | 2.16                     | 9.6 | 1.03                                       | 0.005    | 9.0 |
| 2        | 49.14           | 18.10           | 62.03        | 1.84                     | 6.1 | 0.67                                       | 0.010    | 5.9 |
| 3        | 97.84           | 52.51           | 90.55        | 1.27                     | 1.8 | 1.33                                       | 0.004    | 1.7 |
| 4        | 145.1           | 93.02           | 103.7        | 1.03                     | 1.5 | 1.14                                       | 0.004    | 1.4 |

The experimental data of adsorption kinetics were initially analyzed using the EMTM model, which necessitates determining the  $k_L$  value through the minimization of the objective relationship outlined in Equation (6.18). Likewise, the PVDM model was employed for data interpretation, requiring the values of  $D_{e,p}$  and  $k_L$  for its numerical resolution. Here, the  $k_L$  value obtained from the EMTM model was utilized, and the optimal  $D_{e,p}$  value was determined by minimizing the objective relationship specified in Equation (6.18) to best fit the experimental data of the concentration decay curve. The decay curve data for SMX concentration corresponding to Exp. No. 2 are presented in Figure 8.15, along with the decay curves predicted by the EMTM and PVDM models.

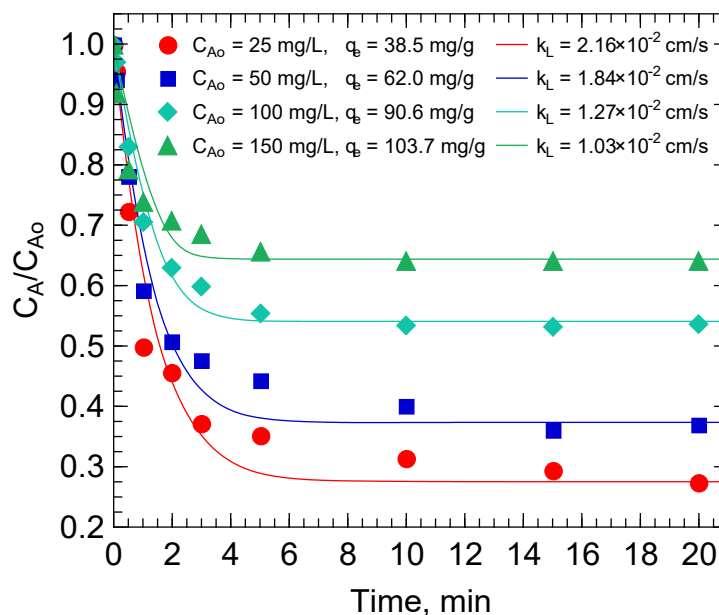
Figure 8.15 depicts the attainment of adsorption equilibrium for SMX on OrganoBent after 15 minutes. The interpretation of the decay curve using the EMTM

model exhibited a satisfactory fit to the experimental data, yielding an optimal  $k_L$  value of  $1.84 \times 10^{-2}$  cm/s and an average percentage deviation of 6.1 %. Conversely, the PVDM model, employing the best  $D_{e,p}$  value of  $0.67 \times 10^{-4}$  cm<sup>2</sup>/s alongside the  $k_L$  value of  $1.84 \times 10^{-2}$  cm/s, reasonably represented the experimental data, with an average percentage deviation of 5.9 %. However, it was observed that  $D_{e,p} = 0.67 \times 10^{-4}$  cm<sup>2</sup>/s is approximately 11.8 times greater than the molecular diffusivity of SMX in diluted solution ( $D_{AB}^0 = 5.66 \times 10^{-6}$  cm<sup>2</sup>/s) estimated using the Wilke-Chang correlation. This discrepancy suggests that the diffusion of SMX in the pore volume occurs 11.8 times faster than its molecular diffusion in solution, which is not feasible. Consequently, it is inferred that external mass transport governs the overall adsorption rate of SMX on OrganoBent. In essence, the external mass transport of SMX from the bulk solution to the external surface of OrganoBent is considerably slower than the intraparticle diffusion of SMX within the pores of OrganoBent.



**Figure 8.15.** Concentration decay curves of SMX during adsorption on OrganoBent at  $C_{A0} = 50$  mg/L and  $T = 25$  °C, for Exp. No. 2. The lines represent the predictions of the EMTM and PVDM models.

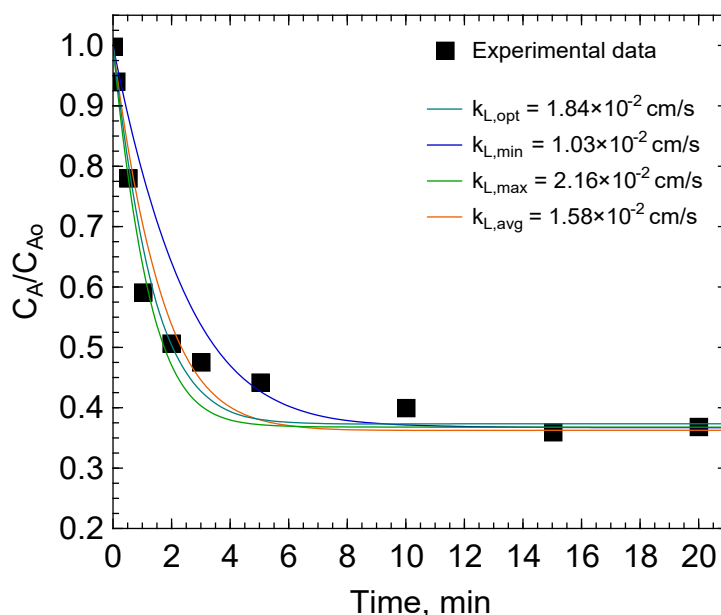
The effect of the uptake adsorbed of SMX on equilibrium ( $q_e$ ) on  $k_L$  was studied by obtaining experimental data of concentration decay while varying the initial concentration of SMX. This effect is depicted in Figure 8.16.



**Figure 8.16.** Concentration decay curves of SMX during adsorption on OrganoBent at  $T = 25\text{ }^{\circ}\text{C}$ , for Exp. Nos. 1-4. The lines represent the prediction of the EMTM model.

In Figure 8.16, it is evident that the EMTM model satisfactorily interpreted the experimental data. The calculated values of  $k_L$  are detailed in Table 8.7, ranging from  $1.03 \times 10^{-2}$  to  $2.16 \times 10^{-2}$  cm/s, and they slightly decrease as  $q_e$  increases. This latter result is unexpected, as  $k_L$  should depend solely on the hydrodynamics of the system and not on the uptake adsorbed. Leyva-Ramos et al. (2012) studied the adsorption rate of pyridine and phenol on cloth-type activated carbon fiber and found that external mass transport controls the overall adsorption rate. The values of  $k_L$  varied in the range of  $0.61 \times 10^{-2}$  to  $2.15 \times 10^{-2}$  cm/s and were independent of the solute concentration.

The sensitivity of the EMTM model to variations in  $k_L$  was assessed by analyzing the experimental data from the SMX concentration decay curve using different  $k_L$  values, as depicted in Figure 8.17.



**Figure 8.17.** Effect of  $k_L$  on the concentration decay curves of SMX during adsorption on OrganoBent at pH = 7 and T = 25 °C, for Exp. No. 2. The lines represent the prediction of the EMTM model.

In Figure 8.17, the curves predicted by the EMTM model are presented with distinct  $k_L$  values:  $1.03 \times 10^{-2}$ ,  $2.16 \times 10^{-2}$ ,  $1.84 \times 10^{-2}$  and  $1.27 \times 10^{-2}$  cm/s. These values, as listed in Table 8.7, represent the minimum ( $k_{L,min}$ ), maximum ( $k_{L,max}$ ), best fit to Exp. No. 2 data ( $k_{L,opt}$ ), and the arithmetic average of all  $k_L$  values from Table 8.7 ( $k_{L,avg}$ ). Notably, the fit of the experimental data for all  $k_L$  values was highly satisfactory, with percentage deviations of 5.4, 6.8, 6.7 and 6.2 % for  $k_{L,min}$ ,  $k_{L,max}$ ,  $k_{L,opt}$  and  $k_{L,avg}$ , respectively. These results indicate that the EMTM model effectively interprets the experimental data for all four experiments using  $k_{L,avg}$ .

## 8.4 Conclusions

In this study, a comprehensive analysis of the adsorption behavior of cation chlorphenamine ( $CPA^+$ ), anion sulfamethoxazole ( $SMX^-$ ), zwitterion tetracycline ( $TC^\pm$ ) and neutral carbamazepine ( $CBZ^0$ ), on hexadecyltrimethylammonium bromide-modified organobentonite was conducted in detail. The results indicated a successful

intercalation of the cationic surfactant within the interlayer space of the clay, leading to the formation of a double layer of molecules arranged in an inclined orientation. This intercalation notably increased the basal space (001) from 1.50 to 1.94 nm. Additionally, the sorption of the cationic surfactant onto the external surface of the clay resulted in the blockage of mesoporosity. Furthermore, it was noted a change in the charge of the clay, transitioning from a negative hydrophilic surface to a positive hydrophobic and organophilic surface.

Analysis of adsorption isotherms revealed distinctive capacities for CPA<sup>+</sup>, TC<sup>±</sup>, SMX<sup>-</sup> and CBZ<sup>0</sup> on both unmodified Bent and OrganoBent. Bent exhibited higher capacities for adsorbing CPA<sup>+</sup> (147.6 mg/g) and TC<sup>±</sup> (188.3 mg/g), but lower capacities for SMX<sup>-</sup> (3.4 mg/g) and CBZ<sup>0</sup> (6.8 mg/g), following the order CPA<sup>+</sup> > TC<sup>±</sup> >> CBZ<sup>0</sup> > SMX<sup>-</sup>. Conversely, OrganoBent displayed elevated adsorption capacities for TC<sup>±</sup> (177.0 mg/g), SMX<sup>-</sup> (113.1 mg/g) and CBZ<sup>0</sup> (47.5 mg/g), but lower for CPA<sup>+</sup> (9.8 mg/g), aligning with the order SMX<sup>-</sup> ≈ TC<sup>±</sup> > CBZ<sup>0</sup> > CPA<sup>+</sup>. These trends highlight the influence of both the ionic charge of the pharmaceutical compound and the surface charge of the adsorbent on adsorption capacities, with electrostatic attractions playing a predominant role in both adsorption mechanisms in bentonite and organobentonite.

The evaluation of adsorption capacity for neutral pharmaceutical compounds, MNZ<sup>0</sup>, ACE<sup>0</sup>, CBZ<sup>0</sup>, CPA<sup>0</sup> and TMP<sup>0</sup>, on OrganoBent revealed a linear dependence on Log D values, indicative of solute hydrophobicity. Adsorption capacity decreased in the order: CPA<sup>0</sup> > CBZ<sup>0</sup> > TMP<sup>0</sup> > ACE<sup>0</sup> > MNZ<sup>0</sup>, consistent with decreasing Log D values. This highlights the significant contribution of hydrophobic partitioning between the solution and the alkyl chains of the surfactant to the adsorption mechanisms. The effect of solution pH, ionic strength and temperature demonstrated a high dependence of adsorption capacity on solution pH and ionic strength, while temperature exerted negligible influence.

Concentration decay curves were adequately interpreted by the EMTM and PVDM models and the results revealed that external mass transport controls the overall adsorption rate on OrganoBent, indicating slower external mass transport of the



pharmaceutical compound compared to intraparticle diffusion within the pores of OrganoBent.

# CHAPTER

# 9

**SYNTHESIS OF POROUS  
CARBON XEROGEL  
ADSORBENTS WITH TAILORED  
HIERARCHICAL POROSITY AND  
MORPHOLOGY FOR THE  
SELECTIVE REMOVAL OF  
SULFAMETHOXAZOLE FROM  
WATER**

## **9.1 Introduction**

The rapid global expansion and uncontrolled development of anthropogenic activities have led to a novel class of hazardous pollutants known as emerging contaminants (Mishra et al., 2023). Pharmaceutical compounds fall within this category and have become a significant global concern due to their crucial environmental and human health risks, particularly when found in water sources, even at low concentrations (Hejna et al., 2022).

Sulfamethoxazole (SMX) is one of the most common sulfonamides bacteriostatic antibiotics frequently used to inhibit dihydropteroate synthase, a precursor of folic acid involved in bacterial growth. Due to growth bacterial resistance against SMX, it is often administered in combination with trimethoprim. The extensive use of SMX has resulted in its detection in various water sources, with concentrations ranging from 0.002 to 11.25 µg/L in surface water (Bagnis et al., 2020; Čelić et al., 2019; Hernández-Tenorio et al., 2022), from 0.127 to 27.41 µg/L in groundwater samples (Karimi et al., 2023; Kibuye et al., 2019; Bexfield et al., 2019), from 0.044 to 0.089 µg/L in drinking water (Inreiter et al., 2016) and even from 3 to 56 µg/L in wastewater samples (Kairigo et al., 2020).

According to the US Geological Survey, SMX ranks among the 30 most frequently detected wastewater contaminants (Grenni et al., 2019). The increasing contamination with SMX arises from its increased consumption and the inefficiencies of conventional wastewater treatment methods in effectively removing this compound. Adsorption is a promising method extensively employed to remove pharmaceutical compounds from water. A diverse range of adsorbents, particularly carbon-based materials derived from biomass, have been applied in this process. Zhang et al. (2020) studied the adsorption of SMX on magnetic biochars, reporting a maximum adsorption capacity of 187.31 mg/g. Similarly, Tan et al. (2022) utilized biochar derived from microalgal biomass residues, achieving an adsorption capacity of 287.89 mg/g. The granular activated carbon known as F400 exhibited an adsorption capacity of 400 mg/g at pH = 3 and 25 °C (Moral-Rodríguez et al., 2016). In contrast, Hou et al. (2023) employed a ZnCl<sub>2</sub>-modified biochar with hierarchical pore structures, reaching an

impressive adsorption capacity of 597.57 mg/g. Prasannamedha et al. (2021) also utilized a biochar derived from sugarcane bagasse with an adsorption capacity of 400 mg/g. Other carbonaceous materials such as ordered mesoporous carbon (334 mg/g) (Sarker et al., 2023), magnetic activated carbon nanocomposite (72.46 mg/g) (Ghate et al., 2021) and powdered activated carbon embedded chitosan-polyvinyl alcohol composite beads have also been applied for adsorbing SMX (9.1 mg/g) from aqueous solutions (Zhou et al., 2020).

Initially developed by Pekala (1989), carbon gels are nanostructured materials synthesized through the polymerization sol-gel process of a hydroxylated benzene derivative and an aldehyde. These materials present significant advantages over activated carbons and other porous carbon materials because their chemical composition, particle size and pore size distribution can be designed and controlled. The properties of carbon gels can be tailored to specific applications by adjusting the chemical conditions involved during the synthesis process, including pH, dilution ratio, type of solvent, type of monomer, type of catalyst, temperature, drying method and carbonization and activation conditions (Bailón-García et al., 2020; Elmouwahidi et al., 2021; Fairén-Jiménez et al., 2008; Ramírez-Valencia et al., 2023).

The research on tailoring the properties of carbon xerogel materials to enhance their adsorption capacity towards pharmaceutical compounds from water is currently insufficient. Moreover, the investigation of synthesis conditions to precisely adjust pore size distribution for promoting the adsorption capacity and reducing flow resistance towards SMX still needs to be examined. Therefore, in Chapter 9, carbonaceous adsorbents were synthesized through sol-gel polymerization of resorcinol (R) and formaldehyde (F), using  $\text{Cs}_2\text{CO}_3$  (Cs) as a catalyst for the efficient removal of SMX from water. The synthesis conditions varying the R/Cs ratio were meticulously optimized to tailor the textural, chemical, mechanical, and morphological properties, aiming to maximize the capacity for adsorbing SMX. The adsorption isotherms of SMX on the adsorbents were obtained, and a comprehensive analysis was conducted to assess the effect of different operating conditions, such as the R/Cs ratio, pH, ionic

strength and solution temperature, on adsorption capacity. Additionally, the adsorption mechanisms were elucidated based on experimental findings.

## **9.2 Experimental methodology**

### **9.2.1 Synthesis of nanostructured carbon xerogels**

Nanostructured carbon xerogel adsorbents (CXCs) were synthesized through a sol-gel polymerization process involving resorcinol and formaldehyde, with  $\text{Cs}_2\text{CO}_3$  as a catalyst. Solutions of resorcinol (R), formaldehyde (F), water (W) and  $\text{Cs}_2\text{CO}_3$  (Cs) were formulated in specified molar ratios ( $\text{R/F} = 1/2$  and  $\text{R/W} = 1/15$ ). The porosity was modulated by varying the R/Cs ratio at values of 100, 500, 1000 and 2000. Additionally, carbon xerogels were synthesized without utilizing a catalyst and were used as a reference material.

The solutions were cast into cylindrical glass molds with 1.8 cm inner diameter (D) and hermetically sealed. The polymerization and curing process involved 1 day at room temperature, followed by 1 day at 50 °C and completed in 5 more days at 80 °C. After curing, the glass molding was removed, the resulting organic polymer was cut to a desired length (L), maintaining an L/D ratio of 1.8, and submersed in a 2 M acetic acid solution for 1 day. Subsequently, the water occupying the porosity was systematically replaced by immersing in acetone for 3 days and changing the acetone solution twice daily to form organic gels. The organic gels were air-dried until constant weight and then carbonized in an  $\text{N}_2$  flow of 150 mL/min for 2 h at 300 °C, followed by an additional 2 h at 850 °C, employing a heating ramp of 1.5 °C/min. Post-carbonization, the obtained carbon xerogels exhibited a 22 % reduction in dimensions, resulting in final dimensions of 1.4 cm diameter and 2.5 cm length. The carbon xerogels were designated as CXC<sub>s</sub>100, CXC<sub>s</sub>500, CXC<sub>s</sub>1000 and CXC<sub>s</sub>2000, according to the R/Cs ratio used in the synthesis process.

### **9.2.2 Characterization techniques**

The textural properties of CXCs were evaluated by analyzing the  $\text{N}_2$  and  $\text{CO}_2$  adsorption isotherms, in addition to Hg intrusion porosimeter curves.  $\text{N}_2$  and  $\text{CO}_2$

isotherms were measured using a Quantachrome analyzer, model Autosorb-6B, while Hg intrusion curves were obtained with a Micromeritics Hg porosimeter, model AutoPore V. The surface area,  $S_{\text{BET}}$ , was determined by applying the Brunauer-Emmet-Teller equation (Brunauer et al., 1938). The volumes of micropores,  $V_{\text{mic}}(\text{N}_2)$  and  $V_{\text{mic}}(\text{CO}_2)$ , were estimated using the Dubinin-Radushkevich equation to the  $\text{N}_2$  and  $\text{CO}_2$  adsorption data, respectively. The mean pore width ( $L_0$ ) and the area of micropores ( $S_{\text{mic}}(\text{N}_2)$ ) were calculated using the Stoeckli equation (Rouquerol et al., 1998). The Hg intrusion curves facilitated the calculation of the mean pore diameter ( $D_p$ ), total pore volume ( $V_p$ ), as well as mesopore volume ( $V_{\text{meso}}(\text{Hg})$ ), macropore volume ( $V_{\text{macro}}(\text{Hg})$ ), mesopore area ( $S_{\text{meso}}(\text{Hg})$ ), macropore area ( $S_{\text{macro}}(\text{Hg})$ ) and external area ( $S_{\text{ext}}(\text{Hg})$ ). Furthermore, these curves allowed the construction of pore size distribution (PSD) curves for micropore, mesopore and macropore regions.

The morphological characteristics of CXCs were examined through scanning electron microscopy at different magnifications using an FEI microscope, model Quanta 400. The mechanical properties of CXCs were assessed through compression experiments using a universal precision tester, Shimadzu AGS-J 10 kN, with a deformation velocity of 0.5 mm/min. The length/diameter ratio of the CXC samples was maintained at 0.7. The compression stress-strain curves were utilized to determine the Young Modulus ( $E$ ), maximum strength ( $\sigma_{\text{max}}$ ) and deformation capacity ( $\epsilon$ ).

The Bohem titration method was employed to analyze the acid-base surface properties of the materials (Boehm, 1966). The total acidic sites were neutralized with NaOH (0.01 N), while the basic sites were neutralized with HCl (0.01 N). The procedure involved adding 45 mL of neutralizing solutions of NaOH (0.01 N) or HCl (0.01 N) to plastic tubes containing 0.15 g of CXC samples. These tubes were then placed in a water thermostatic bath for 5 days with continuous shaking. After this period, 20 mL of each solution was filtered and titrated accordingly with NaOH (0.01 N) or HCl (0.01 N). The concentrations of acidic and basic sites were estimated using the following equations:

$$C_{\text{s,act}} = \frac{V_i}{m} (C_i - C_f) \times 1000 \quad (9.1)$$

$$C_f = \frac{V_T C_T}{V_m} \quad (9.2)$$

where  $C_{s,act}$  is the concentration of acidic-basic sites, meq/g;  $V_i$  is the initial volume of the neutralizing solution, L;  $m$  is the mass of CXCs, g;  $C_i$  is the initial concentration of the neutralizing solution, eq/L;  $C_f$  is the final concentration of the neutralizing solution, eq/L;  $V_T$  is the required volume of the titrated solution, L;  $V_m$  is the volume of the sample of the neutralizing solution, L;  $C_T$  is the concentration of the titrated solution, eq/L.

As described below, the surface charge distribution and the point of zero charge ( $pH_{PZC}$ ) of CXCs were determined using the acid-base titration method proposed by Babić et al. (1999). 21 neutralizing solutions were prepared by mixing different aliquots of NaOH (0.1 N) and HCl (0.1 N) in 50 mL volumetric flasks, standardized with a solution of NaCl (0.1 N), resulting in neutralizing solutions with pH spanning from 2 to 12. In each case, 20 mL of the neutralizing solution was added to centrifuge tubes containing 0.1 g of CXCs, and the remaining solution served as a reference. These tubes were then placed in a water thermostatic bath for 5 days with continuous shaking. Subsequently, the final pH of both the reference solutions and those containing CXCs was plotted against the corresponding volume of the titrated solution. The  $pH_{PZC}$  was the pH at which the curves of the reference and the CXCs intersect. Additionally, the surface charge distribution was calculated as a function of solution pH using the subsequent equations:

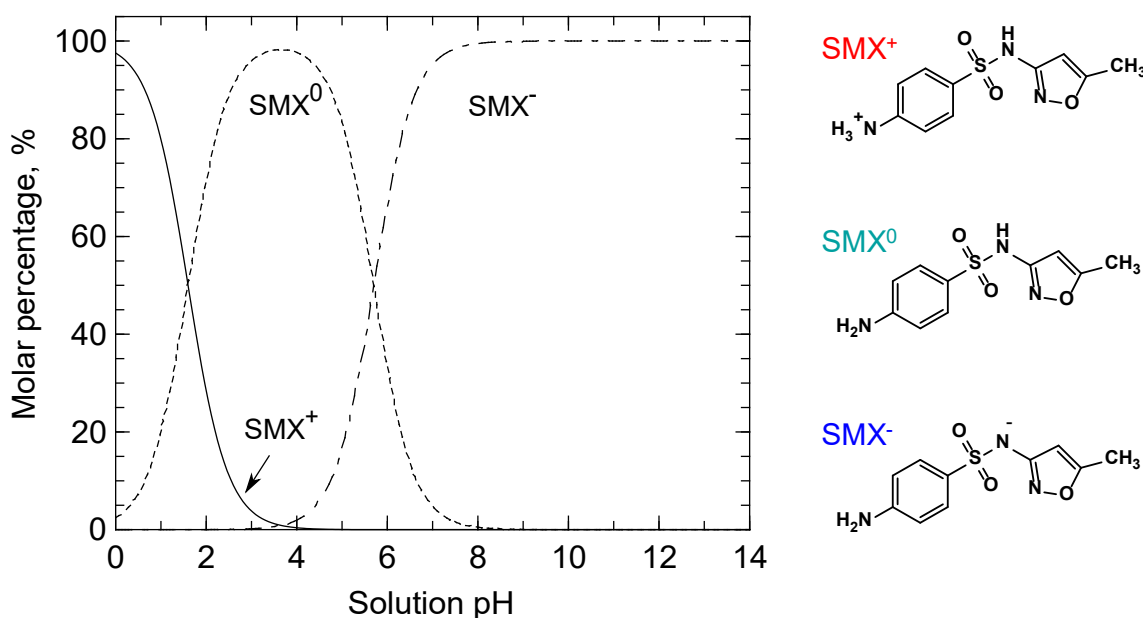
$$C_s = \frac{q_{H^+} F}{m} \quad (9.3)$$

$$q_{H^+} = \frac{C_N (V_B - V_A)}{m} \quad (9.4)$$

where  $C_s$  is the surface charge of CXCs, C/g;  $q_{H^+}$  is the moles of protons adsorbed at a specific pH value, mol/g;  $F$  is the Faraday constant, 96485 C/mol;  $C_N$  is the initial concentration of the neutralizing solution, mol/L;  $V_A$  is the volume of HCl or NaOH required to achieve a specific pH value corresponding to the curve of the solution containing CXCs, L;  $V_B$  is the volume of HCl or NaOH required to achieve a specific pH value corresponding to the reference curve, L.

### 9.2.3 Pharmaceutical compound and quantification

Sulfamethoxazole (SMX) was supplied by Merck, and its physicochemical properties are listed in Table 9.1. In aqueous environments, SMX exhibits various ionic forms contingent upon solution pH. Figure 9.1 illustrates the chemical species distribution at a total SMX concentration of 130 mg/L. The graph indicates that SMX predominantly exists in a cationic species  $\text{SMX}^+$  at pH values below 1.6, where the amino group of the aniline ring accepts a proton. The neutral chemical species  $\text{SMX}^0$  is prevalent between pH 1.6 and 5.7, while the anionic species  $\text{SMX}^-$  predominates at pH values above 5.7 due to the amide group donating a proton. The SMX molecule is a strong  $\pi$ -acceptor because of its amino functional groups and N-heteroaromatic rings (Zheng et al., 2013).

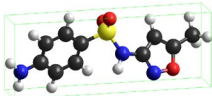


**Figure 9.1.** Chemical speciation diagram of SMX in aqueous solution at a total concentration of 130 mg/L.

The SMX concentrations in aqueous solutions were quantified in a Shimadzu UV-Vis spectrophotometer, model 2600i, and the absorbance was measured at a wavelength of 264 nm. Concentrations were calculated from calibration curves fixed using standard SMX solutions with concentrations ranging from 1 to 20 mg/L.



**Table 9.1.** Physicochemical properties of SMX.

| Pharmaceuticals                            | Family      | Molecular structure <sup>a</sup>                                                  | Molecular size <sup>a</sup><br>(nm) | Log D <sup>b</sup> | pK <sub>a</sub> <sup>c</sup> |
|--------------------------------------------|-------------|-----------------------------------------------------------------------------------|-------------------------------------|--------------------|------------------------------|
| Sulfamethoxazole<br>(SMX)<br>M.W. = 253.28 | Antibiotics |  | X = 1.23<br>Y = 0.46<br>Z = 0.24    | 0.14               | 1.60, 5.70                   |

<sup>a</sup> Determined by Density Functional Theory (DFT) using 6-31G B3LYP method.

<sup>b</sup> Distribution coefficients at pH = 7.

<sup>c</sup> Dissociation constants.

## 9.2.4 Procedure for obtaining adsorption equilibrium data

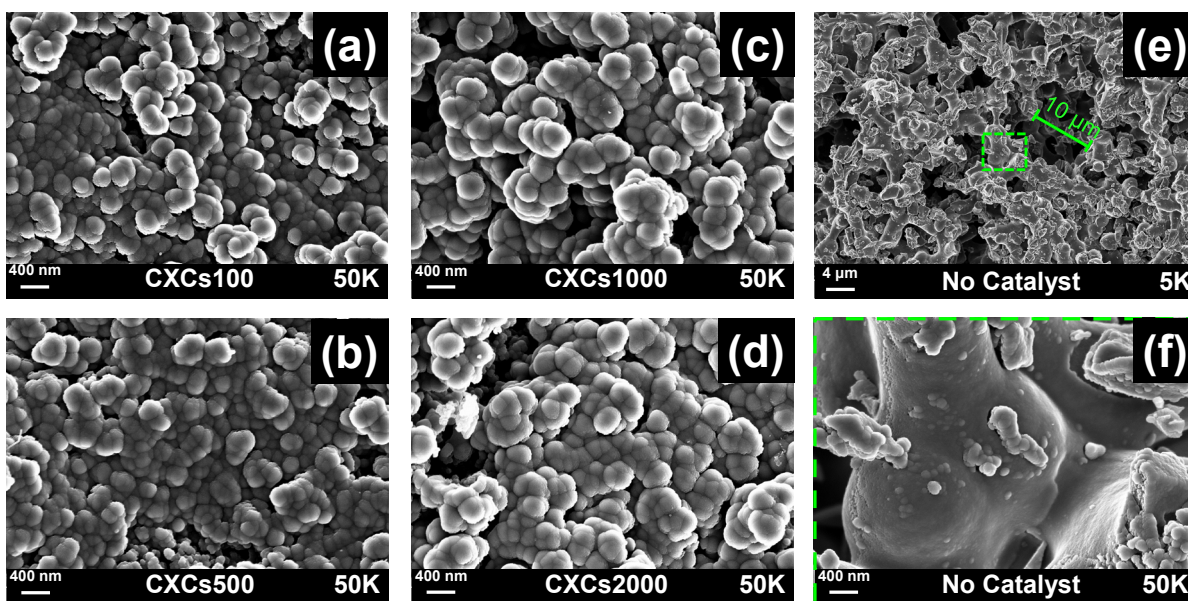
Adsorption equilibrium data were obtained in accordance with the methodology described in Chapter 4, Section 4.2.5, using the batch adsorbents illustrated in Figure 4.2. Adsorption isotherms were derived by graphing  $q$  vs.  $C_{Ae}$ . The operational parameters in the adsorption isotherms encompassed the R/Cs ratio, solution pH, ionic strength and temperature.

## 9.3 Results and discussion

### 9.3.1 Morphological properties

Figure 9.2 shows the SEM images of CXCs at different R/Cs ratios alongside the synthesized sample without a catalyst. At a magnification of 50 K (Figures 9.2 (a) to 9.2 (d)), distinct spherical primary particles are discernible and intricately interconnected to create three-dimensional networks or particle clusters, contributing to developing a coral-like porous structure in these materials. Furthermore, it can be observed that there is a relation between the size of these particle clusters and the R/Cs ratio. As the R/Cs ratio increases, there is an evident trend of enlarging primary particle sizes. This phenomenon can be due to reducing the amount of catalyst, resulting in fewer nucleation centers and promoting the formation of larger particles. For example, in the CXC<sub>s</sub>2000 sample, particle clusters exhibit a notably high size, leading to larger interparticle spaces. Conversely, in the CXC<sub>s</sub>100 sample, primary

particles are smaller, resulting in reduced interparticle sizes compared to the CXCs2000 sample. The remaining samples, CXCs500 and CXCs1000, exhibit diverse primary particle sizes, falling within these limits. SEM images at magnifications of 5K and 50K (Figures 9.2 (e) and 9.2 (f), respectively) depict the sample synthesized without using a catalyst. These images reveal the absence of spherical primary particles, instead showing clusters of exceedingly large interconnected macromolecules, resulting in voids between particles of considerable size, approaching 10  $\mu\text{m}$ . These findings highlight the role of  $\text{Cs}_2\text{CO}_3$ -catalyzed polymerization in facilitating the formation of spherical primary particles, whose size can be finely tuned by adjusting the R/Cs ratio.



**Figure 9.2.** SEM images of the CXCs samples at various R/Cs ratios (a-d) and those synthesized without a catalyst (e, f).

### 9.3.2 Textural properties

The porosity of the CXCs samples was analyzed through  $\text{CO}_2$  and  $\text{N}_2$  physisorption, along with Hg porosimetry, with the results depicted in Figure 9.3 and summarized in Tables 9.2 and 9.3. In Figure 9.3 (a), the  $\text{N}_2$  adsorption-desorption isotherm at  $-196.15^\circ\text{C}$  for the sample synthesized without a catalyst exhibited a type

la isotherm, as per the IUPAC classification (Rouquerol et al., 1998), indicating microporous materials ( $< 2$  nm). Conversely, the other CXC samples with varying R/Cs ratios displayed a combination of type Ia and IIb isotherms, revealing the presence of two different pore types. While type Ia isotherm characterizes microporous materials, type IIb indicates macroporous materials ( $> 50$  nm), displaying an absence of a plateau at high  $P/P^0$  values compared to type Ia isotherms (Thommes et al., 2015). Narrow hysteresis loops were observed, suggesting the presence of wide mesopores and macropores in the samples synthesized with different R/Cs ratios. In these samples, macropores originate from interparticle spaces within the three-dimensional network of spherical particles formed during the gelation process, while micropores develop inside these spherical particles during carbonization (Arenillas et al., 2019; Fairén-Jiménez et al., 2008). These characteristics confer a hierarchical porous structure in the adsorbents compared to the sample synthesized without a catalyst. Notably, varying the R/Cs ratio did not significantly impact  $N_2$  adsorption-desorption isotherms, suggesting that differences primarily lie in the macropore region, influenced by primary particle sizes observed in SEM images (Figures 9.2 (a) to 9.2 (d)). Remarkably,  $S_{BET}$  values remained consistent at 551 to 587  $m^2/g$  across the samples due to the significant contribution of micropores to the  $N_2$  adsorption capacity, while the influence of macropores on these values remained relatively low.

The macroporosity of CXCs was assessed using Hg porosimetry, a method involving filling the sample with mercury and applying pressure to force mercury into interparticle voids (Lowell et al., 2004). Figure 9.3 (b) depicts Hg intrusion porosimetry curves across various R/Cs ratios. It is important to note that the Hg porosimetry curve for the sample synthesized without a catalyst could not be determined. The curves exhibit unimodal behavior, indicating a specific controlled porosity with essentially one predominant pore diameter. The predominance of macropores ( $>50$  nm) is evident in PSD curves (Figure 9.3 (d)) for all samples. Significant differences in Hg intrusion pressure and pore diameter were observed in relation to the R/Cs ratio. In the CXCs2000 sample, Hg intrudes at low pressure (approximately 10 MPa), indicating larger pores ( $D_p = 126.6$  nm). Conversely, the CXCs100 sample shows Hg intrusion at

high pressure ( $> 20$  MPa), revealing narrower macropores ( $D_p = 60.7$  nm). The decrease in the R/Cs ratio correlates with increasing Hg intrusion pressure, implying a reduction in macropore diameter. Notably, differences in meso and macropore properties were observed in Table 9.3, with  $V_p$  and  $S_{\text{ext}}(\text{Hg})$  decreasing drastically as the R/Cs ratio increases. These results highlight the adjustability of the pore diameter, enabling the production of pelletized adsorbents with highly accessible macroporosity and reduced flow resistance by varying the R/Cs ratio.

**Table 9.2.** Textural properties of the CXCs samples analyzed through  $\text{CO}_2$  and  $\text{N}_2$  physisorption.

| Samples     | $\text{CO}_2$ isotherm                                   |                                                |                          |                            |                                                             | $\text{N}_2$ isotherm     |                                                            |                                                           |
|-------------|----------------------------------------------------------|------------------------------------------------|--------------------------|----------------------------|-------------------------------------------------------------|---------------------------|------------------------------------------------------------|-----------------------------------------------------------|
|             | $S_{\text{BET}}^{\text{a}}$<br>( $\text{m}^2/\text{g}$ ) | $V_p^{\text{b}}$<br>( $\text{cm}^3/\text{g}$ ) | $D_p^{\text{c}}$<br>(nm) | $L_0(\text{CO}_2)$<br>(nm) | $V_{\text{mic}}(\text{CO}_2)$<br>( $\text{cm}^3/\text{g}$ ) | $L_0(\text{N}_2)$<br>(nm) | $V_{\text{mic}}(\text{N}_2)$<br>( $\text{cm}^3/\text{g}$ ) | $S_{\text{mic}}(\text{N}_2)$<br>( $\text{m}^2/\text{g}$ ) |
| CXCs100     | 551                                                      | 1.352                                          | 60.7                     | 0.58                       | 0.249                                                       | 1.23                      | 0.220                                                      | 360                                                       |
| CXCs500     | 587                                                      | 1.336                                          | 84.7                     | 0.57                       | 0.248                                                       | 1.13                      | 0.234                                                      | 415                                                       |
| CXCs1000    | 565                                                      | 1.322                                          | 91.2                     | 0.57                       | 0.249                                                       | 1.14                      | 0.226                                                      | 397                                                       |
| CXCs2000    | 573                                                      | 1.271                                          | 126.6                    | 0.60                       | 0.269                                                       | 1.02                      | 0.228                                                      | 446                                                       |
| No Catalyst | 740                                                      | 0.311 <sup>d</sup>                             | 1.68 <sup>e</sup>        | 0.61                       | 0.315                                                       | 0.72                      | 0.293                                                      | 811                                                       |

<sup>a</sup> Specific surface area determined by the BET method.

<sup>b</sup> Total pore volume evaluated by the Hg porosimetry.

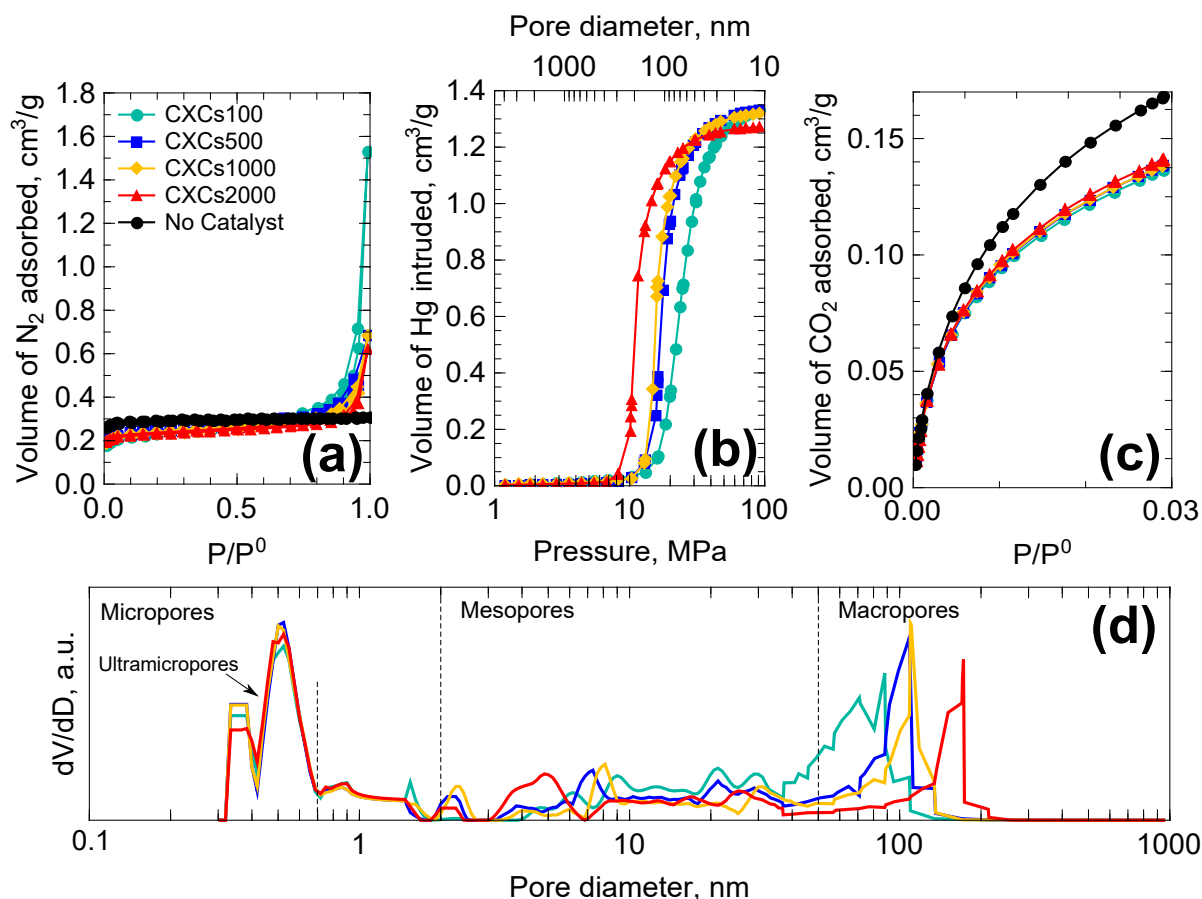
<sup>c</sup> Mean pore diameter obtained by the Hg porosimetry.

<sup>d</sup> Total pore volume estimated by the Gurvich rule at  $P/P^0 = 0.99$ .

<sup>e</sup> Mean pore diameter calculated by the equation  $D_p = (4 \times V_p)/S_{\text{BET}}$ .

**Table 9.3.** Textural properties of the CXCs samples analyzed through Hg porosimetry.

| Samples     | Hg porosimetry                                             |                                                           |                                                             |                                                            |                                                          |
|-------------|------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------|----------------------------------------------------------|
|             | $V_{\text{meso}}(\text{Hg})$<br>( $\text{cm}^3/\text{g}$ ) | $S_{\text{meso}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) | $V_{\text{macro}}(\text{Hg})$<br>( $\text{cm}^3/\text{g}$ ) | $S_{\text{macro}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) | $S_{\text{ext}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) |
| CXCs100     | 0.277                                                      | 34.5                                                      | 1.075                                                       | 55.0                                                       | 89.5                                                     |
| CXCs500     | 0.091                                                      | 11.5                                                      | 1.245                                                       | 51.7                                                       | 63.3                                                     |
| CXCs1000    | 0.098                                                      | 11.7                                                      | 1.224                                                       | 46.6                                                       | 58.3                                                     |
| CXCs2000    | 0.048                                                      | 5.8                                                       | 1.223                                                       | 34.5                                                       | 40.3                                                     |
| No Catalyst | -                                                          | -                                                         | -                                                           | -                                                          | -                                                        |



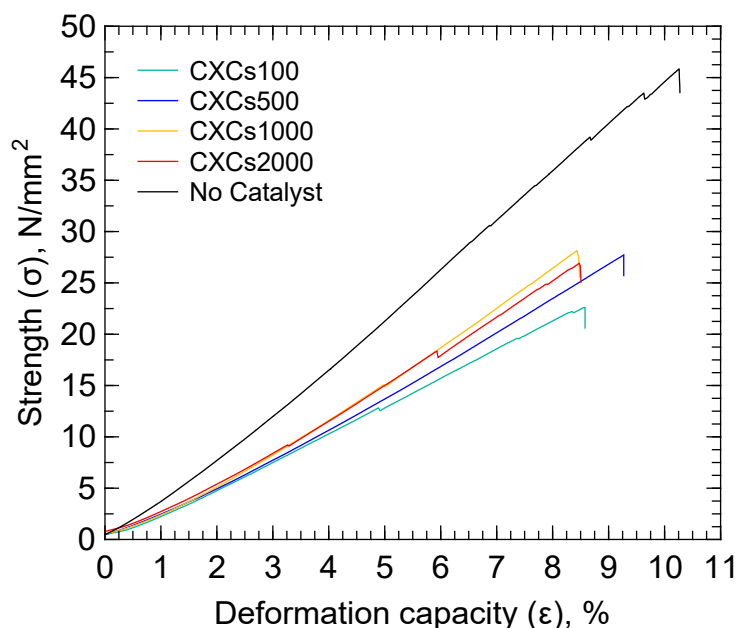
**Figure 9.3.** N<sub>2</sub> adsorption-desorption isotherms at -196.15 °C (a), Hg intrusion porosimetry curves (b) and CO<sub>2</sub> adsorption isotherms at 0 °C (c) of the CXC samples. PSD curves of CXC obtained by NLDFT, QSDFT and Hg porosimetry calculations (d).

Microporosity analysis was conducted using CO<sub>2</sub> adsorption isotherms at 273 K. Figure 9.3 (c) displays these isotherms, revealing a slight decrease in the volume of CO<sub>2</sub> adsorbed upon adding Cs<sub>2</sub>CO<sub>3</sub> catalyst to the reaction. However, negligible influence was observed on micropore development with varying R/Cs ratios. Micropore sizes across samples with distinct R/Cs ratios were consistently ultramicropores (< 0.7 nm), as depicted in Figure 9.3 (d). Moreover,  $V_{\text{mic}}(\text{CO}_2)$  and  $V_{\text{mic}}(\text{N}_2)$  remained similar among these samples, showing no trend with the R/Cs ratio. The mean pore size in the micropore region varied slightly between 0.58-0.60 nm ( $L_0(\text{CO}_2)$ ) and 1.02-1.23 nm

( $L_0(N_2)$ ). The differences between  $L_0(N_2)$  and  $L_0(CO_2)$  were attributed to the failure of  $N_2$  to penetrate narrow micropores at  $-196.15\text{ }^\circ\text{C}$ .  $S_{mic}(N_2)$  values remained stable, ranging from 360 to 446  $\text{m}^2/\text{g}$ , reflecting that the R/Cs ratio impacted primary particle and macropore sizes, rather than micropores. The uniform carbonization conditions across all samples contributed to this stability.

### 9.3.3 Mechanical properties

The mechanical properties of CXCs were assessed by determining stress-strain curves, as illustrated in Figure 9.4, with the results, including  $E$ ,  $\sigma_{max}$  and  $\epsilon$ , outlined in Table 9.4. In the initial compression stage, a linear relationship between stress and strain was observed, corresponding to the elastic deformation of the material. After reaching  $\sigma_{max}$ , considerable decrease in the  $\sigma$ - $\epsilon$  curves were observed, indicating the fracture of weaker walls before the maximum deformation was reached. After  $\sigma_{max}$ , crack propagation led to a rapid drop in stress. This indicates that the final destruction of the adsorbents is associated with crack propagation, after the material has undergone a certain degree of deformation. Thus, the mechanical properties are controlled by the formation and propagation of these cracks in each piece of adsorbent. The data from Figure 9.4 (Table 9.4) revealed remarkable stiffness in CXCs, as evidenced by  $E$  values ranging from 239.5 to 445.6 MPa. Notably, the rigidity of CXCs exhibited a pronounced dependence on the R/Cs ratio. Increasing the R/Cs ratio, there was a concurrent rise in  $E$ , resulting in higher rigid materials, albeit more fragile. Simultaneously, it was observed that the deformation percentage increased raising the R/Cs ratio and further emphasizing the relationship between synthesis conditions and the mechanical behaviour of CXCs. SEM and Hg porosimetry showed that the primary particle sizes enlarged as the R/Cs ratio increased, with  $V_p$  and  $S_{ext}(\text{Hg})$  decreasing drastically. These decreases make the gels denser and, thus, more rigid. Morales-Torres et al. (2010) reported similar findings on preparing carbon aerogels using catalysts of different sizes, which can be related to the degree of overlap of primary particles and porosity.



**Figure 9.4.** Stress-strain curves of the CXC samples.

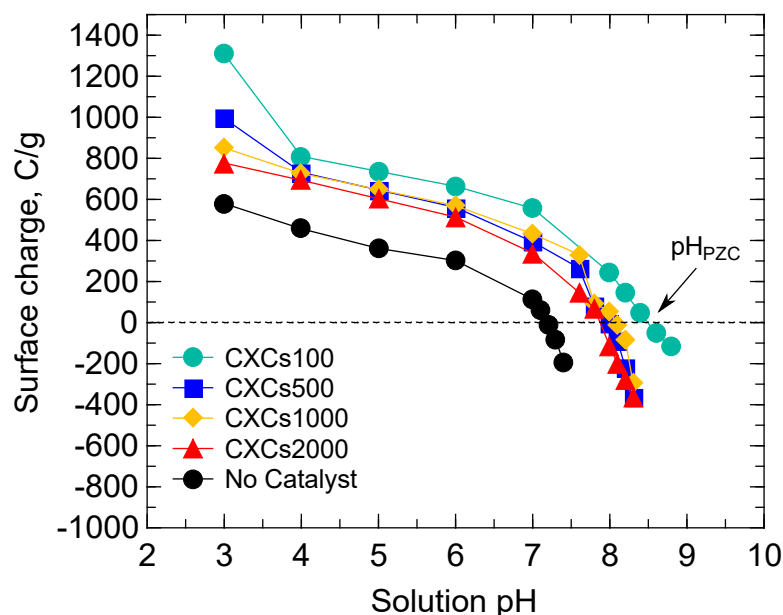
**Table 9.4.** Chemical and mechanical properties of the CXC samples.

| Samples     | Chemical properties        |                           |                   | Mechanical properties   |                                           |                                           |
|-------------|----------------------------|---------------------------|-------------------|-------------------------|-------------------------------------------|-------------------------------------------|
|             | Total acidic sites (meq/g) | Total basic sites (meq/g) | pH <sub>PZC</sub> | Young modulus (E) (MPa) | Maximum strength ( $\sigma_{max}$ ) (MPa) | Deformation percentage ( $\epsilon$ ) (%) |
| CXC100      | 0.36                       | 0.75                      | 8.5               | 239.5                   | 22.60                                     | 8.6                                       |
| CXC500      | 0.38                       | 0.59                      | 8.0               | 315.9                   | 27.72                                     | 9.3                                       |
| CXC1000     | 0.38                       | 0.60                      | 8.1               | 313.0                   | 28.13                                     | 8.4                                       |
| CXC2000     | 0.39                       | 0.59                      | 7.9               | 333.9                   | 26.90                                     | 8.5                                       |
| No Catalyst | 0.36                       | 0.55                      | 7.2               | 445.6                   | 45.83                                     | 10.2                                      |

### 9.3.4 Chemical properties

The surface charge of the CXC samples was analyzed across varying solution pH levels, and the resulting charge distribution is illustrated in Figure 9.5. Additionally, the total acidic and basic sites, along with the pH<sub>PZC</sub> values of the samples, are

recorded in Table 9.4. The graphical representation in Figure 9.5 reveals the  $\text{pH}_{\text{PZC}}$  values of the samples varying from 7.2 to 8.5, indicating a positive surface charge at pH values below  $\text{pH}_{\text{PZC}}$ , transitioning to a negative charge at higher pH values. Interestingly, the addition of  $\text{Cs}_2\text{CO}_3$  catalyst led to a more positive surface charge and consequently increased the  $\text{pH}_{\text{PZC}}$ . However, varying the R/Cs ratio did not result in significant differences in surface charge and  $\text{pH}_{\text{PZC}}$  values, except for the CXCs100 sample. Notably, the chemical nature of CXCs remains predominantly basic, as evidenced by the consistently higher concentration of total basic sites compared to acidic sites across all samples. Moreover, the concentration of total acidic and basic sites remained similar regardless of the R/Cs ratio, except for CXCs100, highlighting that the chemical nature of CXCs is not significantly influenced by variations in the R/Cs ratio.



**Figure 9.5.** Surface charge distribution and  $\text{pH}_{\text{PZC}}$  of the CXCs samples.

### 9.3.5 Adsorption isotherm models

The experimental adsorption equilibrium data of SMX on CXCs from the aqueous phase, under various operating conditions, were effectively modeled using the



Freundlich, Langmuir and Radke-Prausnitz isotherm models, represented by the Equations (4.9-4.11).

Table 9.5 presents the parameters and average percentage deviation of the adsorption isotherms of SMX on CXCs under different operating conditions, including R/Cs ratio, pH, ionic strength and solution temperature. The results indicate that the Freundlich model outperforms the Langmuir model in 11 out of 13 cases, exhibiting lower percentage deviation. Although the Radke-Prausnitz model demonstrates similar deviation percentages to the Freundlich model, the latter yields the lowest %D values in most cases. In this sense, the Freundlich model was selected as the most suitable for interpreting the experimental adsorption equilibrium data of SMX on CXCs under different operating conditions. This model assumes that adsorption occurs on heterogeneous surfaces with multiple layers (Leyva-Ramos, 2010).

**Table 9.5.** Parameters and average percentage deviation of adsorption isotherms of SMX on CXCs at different operating conditions.

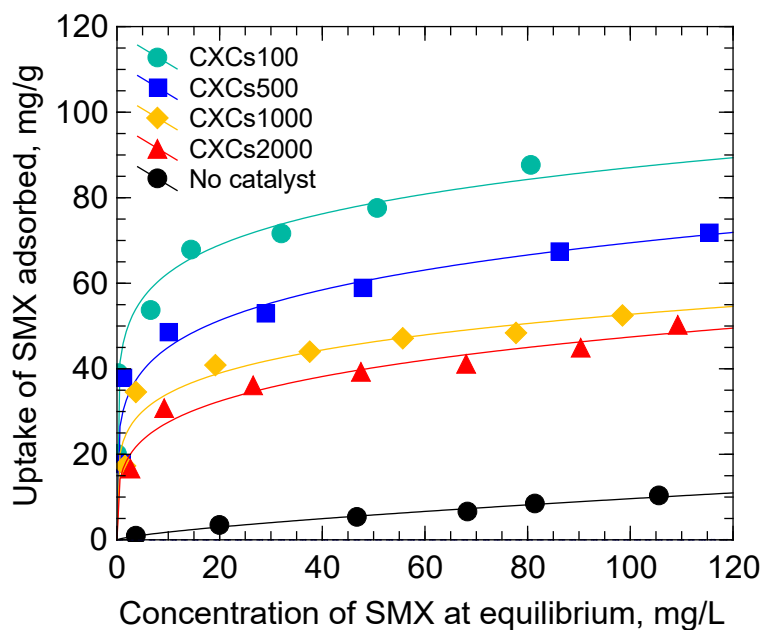
| R/Cs<br>ratio | pH | I<br>(N) | T<br>(°C) | Langmuir        |             |      | Freundlich                                           |     |      | Radke-Prausnitz |                                           |         |      |
|---------------|----|----------|-----------|-----------------|-------------|------|------------------------------------------------------|-----|------|-----------------|-------------------------------------------|---------|------|
|               |    |          |           | $q_m$<br>(mg/g) | K<br>(L/mg) | %D   | k<br>( $\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$ ) | n   | %D   | a<br>(L/g)      | b<br>( $\text{L}^\beta/\text{mg}^\beta$ ) | $\beta$ | %D   |
| *             | 7  | 0.01     | 25        | 26.94           | 0.006       | 14.4 | 0.342                                                | 1.4 | 6.8  | 0.200           | 0.083                                     | 0.55    | 12.0 |
| 100           | 7  | 0.01     | 25        | 72.94           | 4.657       | 11.2 | 44.70                                                | 6.9 | 4.8  | 488.7           | 9.782                                     | 0.88    | 7.8  |
| 500           | 7  | 0.01     | 25        | 63.33           | 0.771       | 13.8 | 29.19                                                | 5.3 | 6.3  | 232.2           | 7.126                                     | 0.84    | 6.9  |
| 1000          | 7  | 0.01     | 25        | 25.57           | 1.403       | 5.2  | 22.20                                                | 5.3 | 4.6  | 861.2           | 38.178                                    | 0.82    | 4.6  |
| 2000          | 7  | 0.01     | 25        | 33.43           | 0.949       | 9.6  | 15.96                                                | 4.2 | 5.1  | 382.6           | 23.697                                    | 0.77    | 5.1  |
| 500           | 3  | 0.01     | 25        | 70.74           | 4.390       | 9.5  | 42.09                                                | 6.5 | 3.2  | 448.2           | 8.674                                     | 0.90    | 5.4  |
|               | 5  | 0.01     | 25        | 61.54           | 1.354       | 6.8  | 35.60                                                | 7.1 | 3.2  | 307.5           | 7.529                                     | 0.89    | 2.5  |
|               | 9  | 0.01     | 25        | 31.29           | 0.388       | 15.2 | 11.64                                                | 4.4 | 7.8  | 121.0           | 9.881                                     | 0.78    | 8.1  |
|               | 11 | 0.01     | 15        | 42.76           | 0.017       | 10.2 | 2.61                                                 | 2.0 | 11.1 | 24.7            | 9.033                                     | 0.50    | 11.1 |
|               | 7  | 0.1      | 35        | 56.12           | 0.627       | 3.5  | 27.27                                                | 5.8 | 6.4  | 60.4            | 1.514                                     | 0.92    | 2.3  |
|               | 7  | 1.0      | 25        | 55.15           | 0.355       | 2.2  | 22.11                                                | 4.6 | 2.2  | 190.2           | 7.840                                     | 0.80    | 1.7  |
|               | 7  | 0.01     | 15        | 63.33           | 0.771       | 20.2 | 27.84                                                | 6.4 | 6.9  | 81.6            | 1.984                                     | 0.94    | 3.7  |
|               | 7  | 0.01     | 35        | 62.35           | 1.740       | 9.6  | 35.15                                                | 6.4 | 4.5  | 500.0           | 13.182                                    | 0.86    | 5.1  |

\* Adsorption isotherm on carbon xerogels synthesized without a catalyst.

### 9.3.6 Effect of resorcinol/catalyst ratio on adsorption capacity for SMX

The effect of the R/Cs ratio on the adsorption isotherms of SMX on CXCs at pH = 7 and T = 25 °C is presented in Figure 9.6. The figure reveals a significant

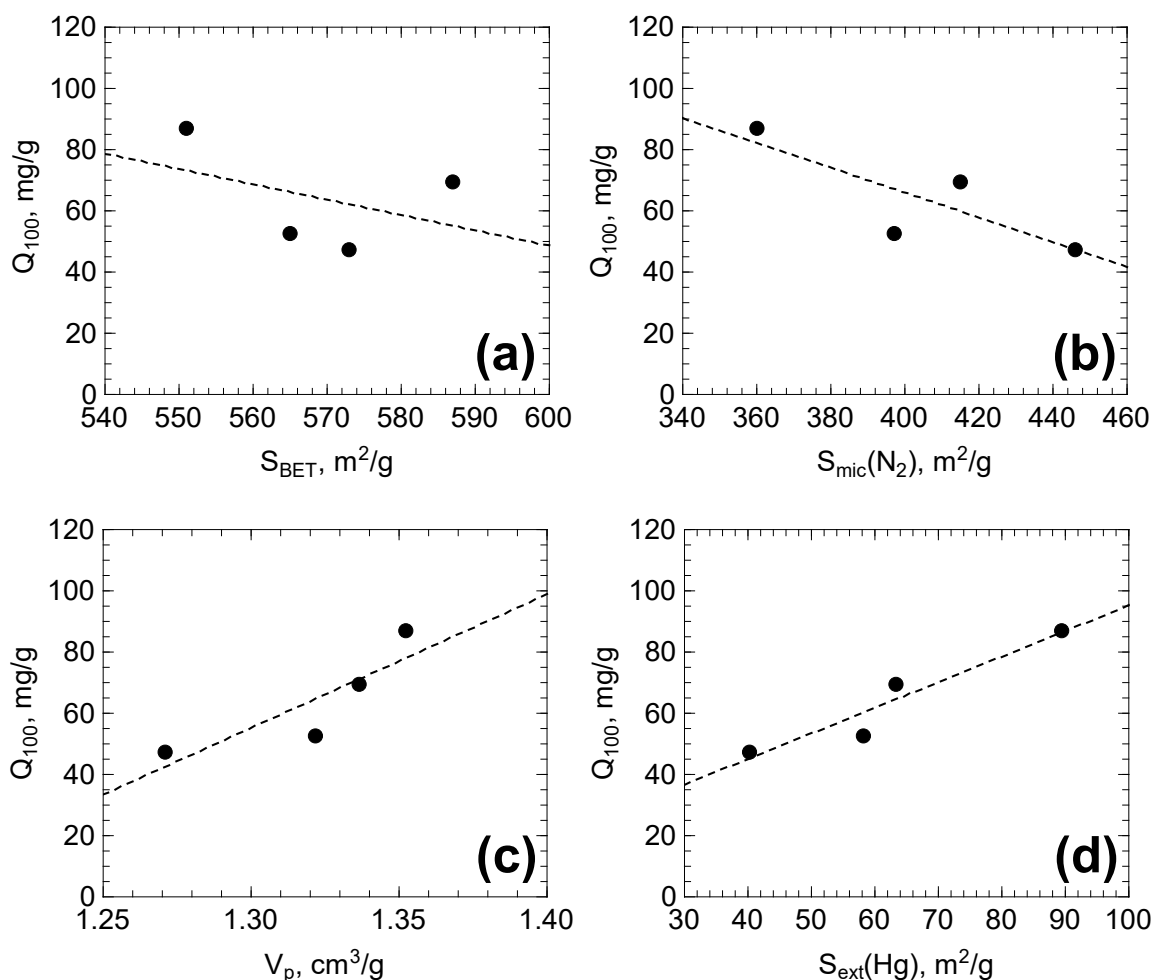
enhancement in the adsorption capacity for SMX when CXCs are catalyzed with  $\text{Cs}_2\text{CO}_3$ . Furthermore, the observed trend indicates a strong dependence of the adsorption capacity on the R/Cs ratio. The highest adsorption capacity for SMX was noted in the CXC<sub>s</sub>100 sample, reaching 87.8 mg/g, followed by a decrement in the following order: CXC<sub>s</sub>100 > CXC<sub>s</sub>500 > CXC<sub>s</sub>1000 > CXC<sub>s</sub>2000 >> No Catalyst. To further assess the impact of the R/Cs ratio, the Freundlich model was utilized to estimate the uptake of SMX adsorbed at a specific equilibrium concentration of 100 mg/L ( $Q_{100}$ ). The results were 87.0, 69.4, 52.7 and 47.4 mg/g for CXC<sub>s</sub>100, CXC<sub>s</sub>500, CXC<sub>s</sub>1000 and CXC<sub>s</sub>2000, respectively, and 9.6 mg/g for the sample without a catalyst. This trend indicates that the adsorption capacity increased 1.83 times as the R/Cs ratio decreased from 2000 to 100 and drastically increased 9.1 times in the CXC<sub>s</sub>100 sample compared to when no catalyst was added.



**Figure 9.6.** Effect of the R/Cs ratio on adsorption isotherms of SMX on CXC<sub>s</sub> at pH = 7 and T = 25 °C. The lines represent the Freundlich isotherm.

### 9.3.7 Effect of textural and mechanical properties on adsorption capacity for SMX

As highlighted earlier, the R/Cs ratio primarily influences the textural, mechanical and morphological properties. Figure 9.7 depicts the influence of selected textural properties ( $S_{\text{BET}}$ ,  $S_{\text{mic}}(\text{N}_2)$ ,  $V_p$  and  $S_{\text{ext}}(\text{Hg})$ ) on the adsorption capacity  $Q_{100}$ .



**Figure 9.7.** Effect of the selected textural properties,  $S_{\text{BET}}$ ,  $S_{\text{mic}}(\text{N}_2)$ ,  $V_p$  and  $S_{\text{ext}}(\text{Hg})$ , on the capacity of CXCs for adsorbing SMX ( $Q_{100}$ ) at pH = 7 and T = 25 °C.

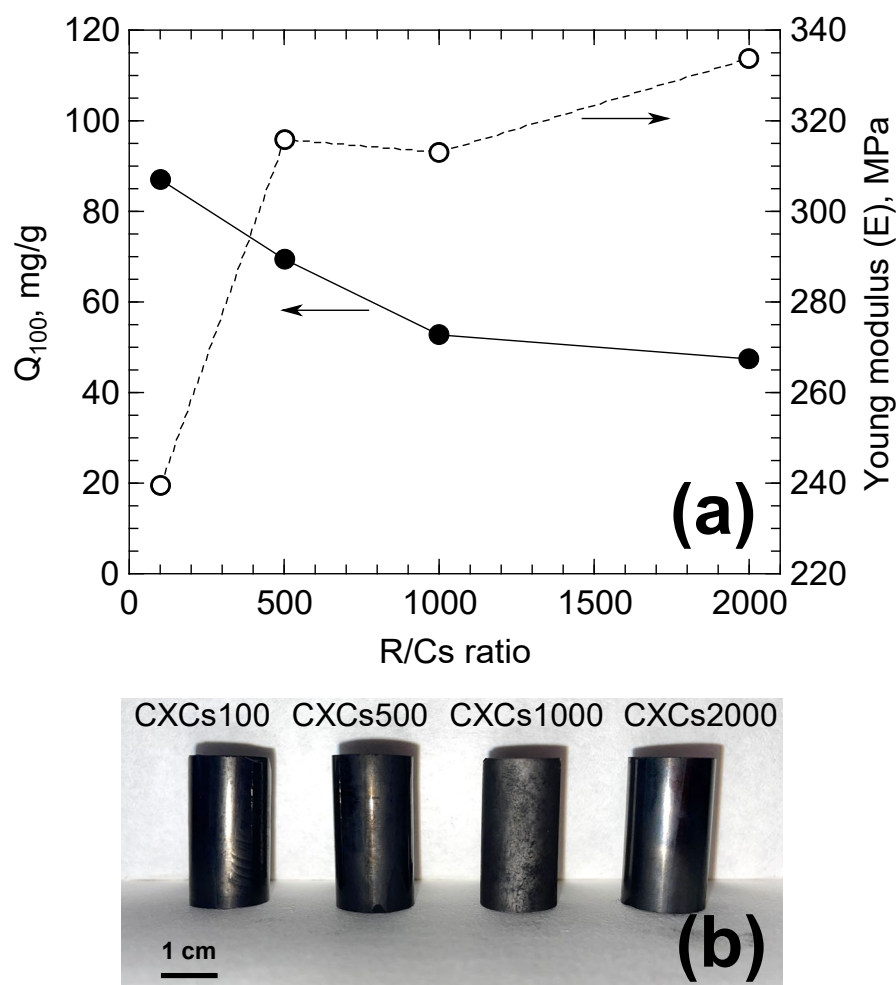
Figure 9.7 (a) reveals that adsorption capacity does not depend on  $S_{\text{BET}}$ , as the experimental data show no discernible trend with increasing  $S_{\text{BET}}$ . Furthermore, Figure 9.7 (b) indicates a decrease in adsorption capacity with increasing  $S_{\text{mic}}(\text{N}_2)$ , suggesting a slight impact of microporosity on adsorption capacity due to the hindered access of

SMX molecules to ultramicropores formed during carbonization. In contrast, Figures 9.7 (c) and 9.7 (d) show the dependence of the adsorption capacity on  $V_p$  and  $S_{ext}(Hg)$ , as estimated through Hg porosimetry. Here,  $V_p$  values, calculated as the sum of  $V_{meso}(Hg)$  and  $V_{macro}(Hg)$ , and  $S_{ext}(Hg)$ , calculated as the sum of  $S_{meso}(Hg)$  and  $S_{macro}(Hg)$ , show a clear tendency of increasing adsorption capacity as these textural properties rise. This outcome suggests that adsorption predominantly occurs in macropores and wide mesopores, controlled by  $\pi$ - $\pi$  dispersive interactions between the  $\pi$ -acceptors present in the functional amino group and N-heteroaromatic ring of SMX and the  $\pi$ -donors within the CXCs.

Figure 9.8 (a) illustrates the variation of adsorption capacity  $Q_{100}$  and  $E$  with the R/Cs ratio. Additionally, Figure 9.8 (b) provides a visual representation of the obtained adsorbents. Despite CXC<sub>s</sub>100 presenting the highest adsorption capacity, the rigidity of the material is notably low, and the presence of fractures along the adsorbent is evident. Conversely, CXC<sub>s</sub>2000 demonstrates higher rigidity but substantially lower adsorption capacity. In this sense, CXC<sub>s</sub>500 was selected as the optimal adsorbent for removing SMX from aqueous solutions, maintaining a favorable adsorption capacity and sufficient rigidity to prevent the crushing of the adsorbent.

### 9.3.8 Effect of pH, ionic strength and temperature on adsorption capacity for SMX

Figure 9.9 presents the effect of solution pH, ionic strength and temperature on the adsorption isotherms of SMX on CXC<sub>s</sub>500, along with the interpretation of experimental data using the Freundlich model. In Figure 9.9 (a), the effect of solution pH was depicted at  $I = 0.01$  N and  $T = 25$  °C. This figure shows a dependence of adsorption capacity on solution pH. The maximum adsorption capacity was 83.8 mg/g at pH = 3, gradually decreasing with increasing solution pH, except at pH = 5 and 7, where the adsorption capacity remained relatively similar. For an equilibrium concentration of 100 mg/L, the uptakes adsorbed predicted by the Freundlich model were 85.5, 68.4, 69.5, 33.4 and 26.6 mg/g for pH values of 3, 5, 7, 9 and 11, respectively.



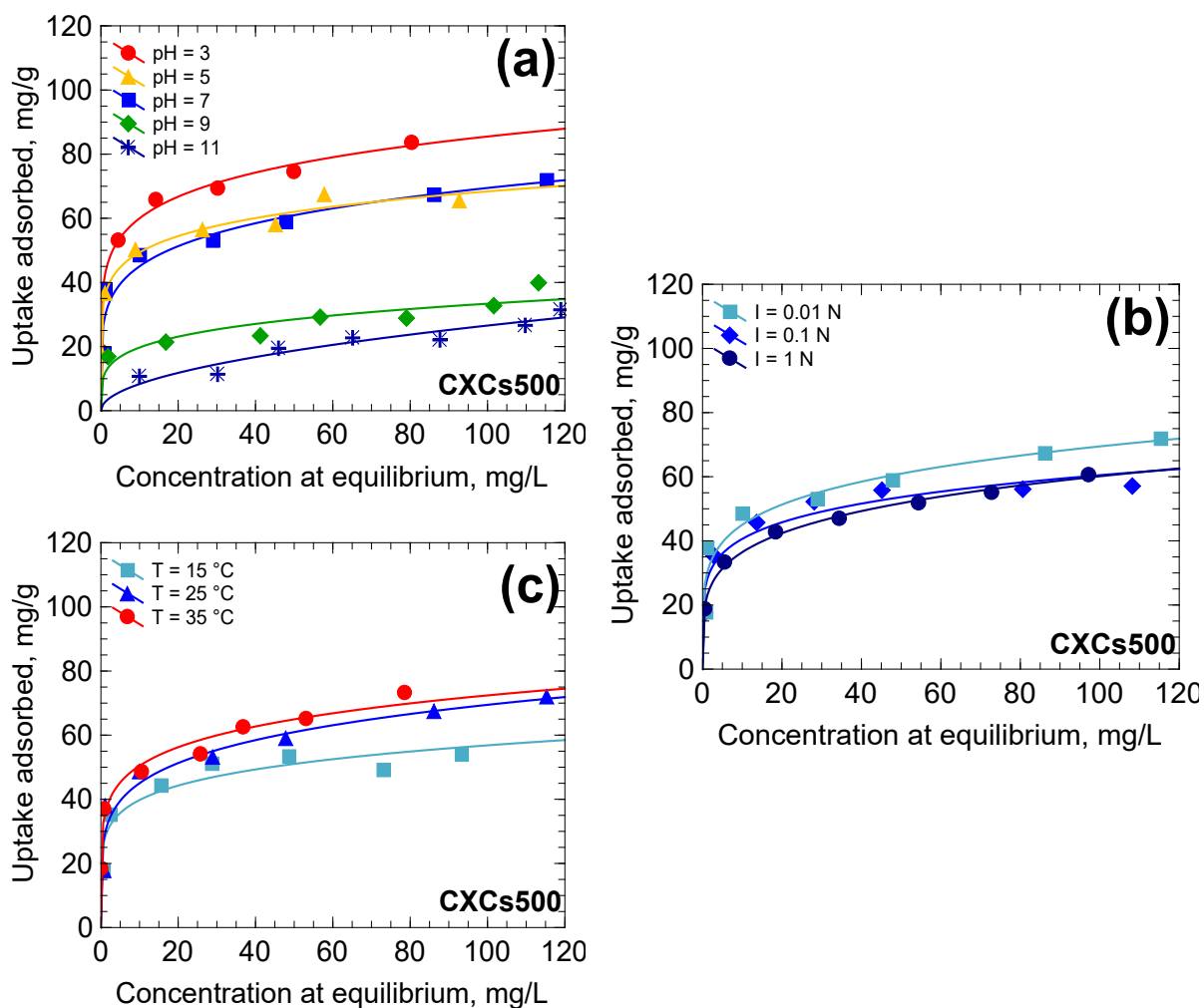
**Figure 9.8.** Variation of the uptake of SMX adsorbed ( $Q_{100}$ ) on CXCs and Young modulus ( $E$ ) with the R/Cs ratio (a). Visual representation of the obtained adsorbents (b).

The pH dependency of adsorption capacity can be attributed to the chemical species of SMX (Figure 9.1) and the surface charge of CXCs500 (Figure 9.5). At pH values below the  $pH_{PZC}$  of CXCs500 (8.0), higher adsorption capacities are driven by electrostatic attraction between the  $SMX^-$  species and the positively charged surface of CXCs500 in addition to  $\pi$ - $\pi$  dispersive interactions. Notably, at  $pH = 3$ , adsorption capacity is fully controlled by  $\pi$ - $\pi$  dispersive interactions, as SMX is present as a neutral species. Conversely, at pH values above the  $pH_{PZC}$ , electrostatic repulsion

occurs between the  $\text{SMX}^-$  and the negatively charged surface of CXC500, resulting in weak  $\pi$ - $\pi$  interactions, substantially reducing adsorption capacity at pH 9 and 11. The enhanced adsorption capacity at pH = 3, compared to pH 5 and 7, can be attributed to the more hydrophobic character of SMX at pH = 3 than at pH 5 and 7, favoring adsorption via  $\pi$ - $\pi$  dispersive interactions. Zhang et al. (2010) investigated the adsorption mechanisms of different SMX species on functionalized carbon nanotubes. They concluded that the adsorption of  $\text{SMX}^0$  is consistently predominant and effectively due to hydrophobic and electron-donor-acceptor interactions.

Figure 9.9 (b) illustrates the impact of solution ionic strength on adsorption capacity at pH = 7 and  $T = 25^\circ\text{C}$ . The figure reveals a slight decrease in adsorption capacity with a 100-fold increase in solution ionic strength from 0.01 to 1 N. For instance, at an equilibrium concentration of 100 mg/L, the uptakes adsorbed predicted by the Freundlich model were 69.5, 60.5 and 60.2 mg/g for ionic strengths of 0.01, 0.1 and 1 N, respectively. This minor reduction (13.4 %) suggests no competition between  $\text{Cl}^-$  ions and  $\text{SMX}^-$  in the solution for the positively charged anionic sites. This result highlights that adsorption via  $\pi$ - $\pi$  dispersive interactions is more significant than electrostatic attraction and explains the highest adsorption capacity at pH = 3, where the  $\text{SMX}^0$  species is predominant in the solution.

The influence of solution temperature on adsorption isotherms of SMX on CXC500 at pH = 7 and  $I = 0.01\text{ N}$  is represented in Figure 9.9 (c). The figure shows an enhancement in adsorption capacity increasing temperature, with the maximum adsorption capacity observed at  $T = 35^\circ\text{C}$ , 73.2 mg/g. For an equilibrium concentration of 100 mg/L, the Freundlich model predicted adsorption capacities of 72.4, 69.5 and 56.8 mg/g at  $T = 35, 25$  and  $15^\circ\text{C}$ , respectively. This tendency reveals a 21.5 % reduction in adsorption capacity when lowering the temperature from 35 to  $15^\circ\text{C}$ . The isosteric heat of adsorption was calculated with Equation (4.13). Considering an uptake of SMX adsorbed of 54.2 mg/g,  $C_{e1} = 25.84\text{ mg/L}$  ( $T_1 = 308.15\text{ K}$ ) and  $C_{e2} = 93.27\text{ mg/L}$  ( $T_2 = 288.15\text{ K}$ ), the calculated  $(\Delta H_{\text{ads}})_q$  was 47.4 kJ/mol, indicating that SMX adsorption on CXC500 is endothermic.



**Figure 9.9.** Effect of solution pH (a), ionic strength (b) and temperature (c) on adsorption isotherms of SMX on CXC500. The lines represent the Freundlich isotherm.

## 9.4 Conclusions

Porous carbon xerogel adsorbents were precisely synthesized with tailored hierarchical pore size distribution to minimize flow resistance, high rigidity, surface chemistry and morphology to remove SMX from water efficiently. This outcome was achieved by adjusting the R/Cs ratio during synthesis. The results demonstrated that the textural, morphological and mechanical properties of the adsorbents can be effectively tuned by varying the R/Cs ratio. An increase in the R/Cs ratio resulted in an

evident enlargement of primary particle sizes, leading to a significant increase in the mean pore diameter within the macropore region while simultaneously reducing the total pore volume and  $S_{\text{ext}}(\text{Hg})$ . Furthermore, the rigidity of the adsorbents increased with higher R/Cs ratios, mitigating the risk of adsorbent breakdown. The surface chemistry of the adsorbents remained consistent across all samples, characterized by a basic nature with a positively charged surface below  $\text{pH} = 8$ .

The adsorption capacity showed a clear dependence on the R/Cs ratio. The maximum adsorption capacity was observed in the CXCs100 sample, reaching 87.8 mg/g, and decreased with increasing R/Cs ratio. The results reveal that SMX predominantly adsorbs onto wide mesopores and macropores through  $\pi$ - $\pi$  dispersive interactions, with the uptake of SMX adsorbed reducing as total pore volume and meso and macropore areas decrease. CXCs500 adsorbent was identified as the optimal synthesis condition for adsorbing SMX, demonstrating a favorable adsorption capacity while preventing adsorbent breakdown. Furthermore, the influence of pH, ionic strength, and solution temperature revealed the presence of weak electrostatic attractions in the adsorption mechanism, in addition to strong  $\pi$ - $\pi$  dispersive and hydrophobic interactions. The increasing adsorption capacity with temperature revealed an endothermic process.



# CHAPTER

# 10

**ADVANCED DESIGN AND  
FABRICATION OF NEW 3D-  
PRINTED CARBON MONOLITH  
ADSORBENTS FOR THE REMOVAL  
OF SULFAMETHOXAZOLE FROM  
WATER: EFFECT OF SYNTHESIS  
CONDITIONS ON THEIR DYNAMIC  
ADSORPTION PERFORMANCE**

## **10.1 Introduction**

Fixed bed adsorption columns are widely used in industry for the removal of various pollutants from wastewater, including toxic heavy metals and hazardous organic compounds (Patel, 2019, 2022). These systems employ a wide range of adsorbent materials, each tailored to specific pollutants. These include biochars (Bazarin et al., 2024; Zoroufchi Benis et al., 2023), biomass-derived materials (Solgi et al., 2023), clay-based materials (Aboussabek et al., 2024), metal-organic frameworks (Sukatis et al., 2024) and carbon-based materials (Allahkarami et al., 2022; Dwivedi et al., 2008; Hameed et al., 2024). The adsorption capacity of these adsorbents in fixed bed columns is strongly influenced by their particle size, chemical composition, morphology, texture and mechanical properties (Leyva-Ramos, 2010). In addition, operational parameters such as feed concentration, bed height, flow rate, pH and temperature significantly affect the adsorption efficiency (Ahmed and Hameed, 2018).

Despite their efficacy, fixed bed adsorbers face significant operational challenges, primarily in achieving optimal packing, bed homogeneity and particle size distribution of the adsorbent within the columns. Inadequate control of these factors can result in adsorbent attrition, channeling, uneven flow distribution, mass transfer limitations, high pressure drops and scalability challenges (Patel, 2019; Thirunavukkarasu et al., 2021), ultimately reducing pollutant removal efficiency. To address these challenges, structured adsorbents are increasingly being explored as alternatives to traditional randomly packed beds.

Monoliths are emerging as highly promising nanostructured porous materials, characterized by a single structure composed of thin, vertical, parallel channels separated by walls and a complex network of macropores that reduce flow resistance (Hosseini et al., 2020). Due to their unique design and structure enable monoliths to effectively mitigate issues related to adsorbent particle arrangement and pressure drops. However, conventional manufacturing methods such as extrusion impose significant limitations by restricting the channel geometry to straight channels (Vergunst et al., 2001). In addition, the porous structure can suffer from imperfections during

manufacturing, resulting in uneven porosity (Govender and Friedrich, 2017). The lack of uniform porosity and precise control over channel geometry limits fluid dynamics to laminar flow within the channels, preventing mixing and distribution of the fluid, and resulting in poor diffusion through of the monolith porosity (Kovacev et al., 2021). Consequently, these limitations result in minimal adsorbate-adsorbent interaction and the creation of preferential flow paths that compromise pollutant removal efficiency. Beckwée et al. (2022) studied the dynamic adsorption of n-butanol from aqueous phase on activated carbon monoliths and observed instantaneous column breakthrough with a broadening breakthrough curve. The authors attributed this phenomenon to channeling effects caused by the channel geometry and poor adsorbate-adsorbent interaction.

The recent explosion of techniques integrating sol-gel polymerization with 3D printing technology for the fabrication of 3D-printed carbon monoliths for gas-phase applications has, for the first time, introduced a new paradigm for the creation of precisely ordered three-dimensional packed beds for liquid-phase adsorption purposes (Chaparro-Garnica et al., 2021b, 2022; Parra-Marfil et al., 2024). Sol-gel polymerization allows the synthesis of carbon materials with a precisely tailored chemical composition, particle size, pore size distribution, shape and mechanical strength by modulating synthesis conditions (Pekala, 1989). Concurrently, 3D printing technology enables the design and creation of extremely complex channel geometries with precise control over size, shape, alignment and configuration (Praveena et al., 2022). This innovative approach has the potential to transform fixed bed adsorption systems and offers a promising solution to the limitations of traditional packed bed adsorbents. By tailoring the internal structure of the adsorbent, this approach enhances control over fluid dynamics and mass transport properties, thereby improving adsorption efficiency and operational stability.

This innovative method represents a pioneering advancement in the literature, as no prior studies have successfully integrated these techniques for developing 3D-printed monolithic beds for liquid-phase adsorption. In this sense, Chapter 10 aims to fabricate novel integral 3D-printed carbon monolith adsorbents with varied channel

geometries and porous textures. The method involves sol-gel polymerization of resorcinol (R), formaldehyde (F), water (W) and  $\text{Cs}_2\text{CO}_3$  (Cs) as a catalyst, with advanced 3D printing technology. These adsorbents target the removal of sulfamethoxazole from water, a hazardous antibiotic frequently found in water (Grenni et al., 2019), in both batch and continuous systems. The study evaluates the impact of synthesis conditions on the morphological, textural, chemical and mechanical properties of the monoliths by varying the R/Cs ratio. Additionally, the research investigates how these synthesis conditions affect batch and dynamic adsorption performances. The influence of channel geometry is assessed through breakthrough curves.

## **10.2 Experimental methods**

### **10.2.1 Design and printing of Computer-Aided Design 3D templates**

The 3D templates with specific channel geometries were strategically designed using SolidWorks software, ensuring precision and detail. Two distinct types of CAD 3D templates were designed and are illustrated in Figure 10.1, offering various perspectives including side, top and bottom views. Figure 10.1 (a) illustrates a 3D template with interconnected channels along multiple directions, creating a complex network that resembles a labyrinth with pathways traversing vertically and horizontally. This is similar to an array of interconnected arrows. In contrast, Figure 10.1 (b) presents channels arranged in a conventional linear pattern, aligning primarily along the y-direction, similar to conventional monoliths manufactured by extrusion. These sophisticated templates were then materialized using an Ultimaker 3D printer, model S3, employing a co-polyester transparent filament for optimal fidelity and clarity.

### **10.2.2 Fabrication of 3D-printed carbon monolith adsorbents**

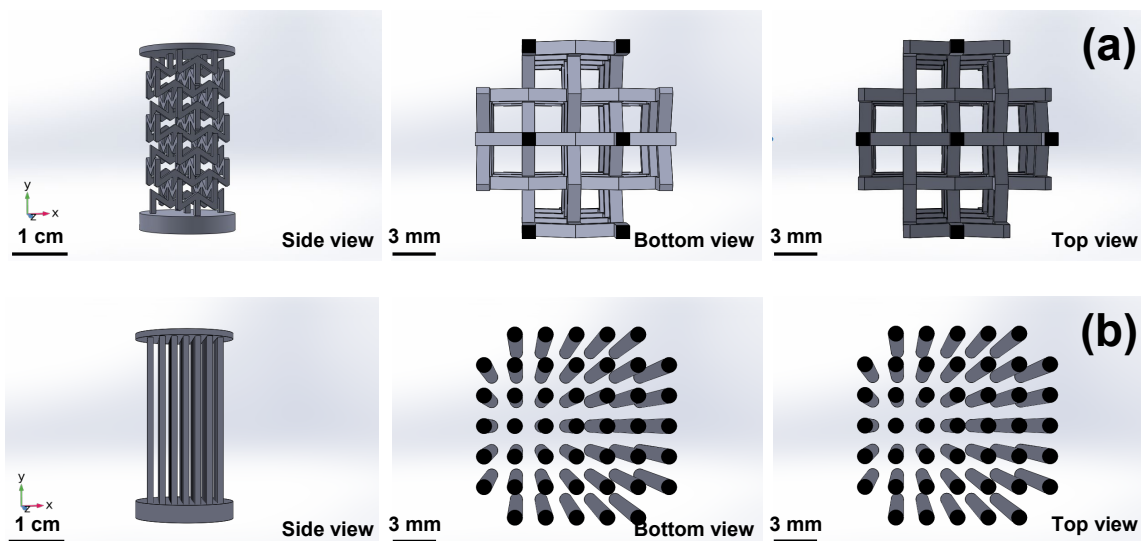
The fabrication process of the 3D-printed carbon monoliths was accomplished through an innovative hybrid method, integrating sol-gel polymerization with advanced 3D printing technology. Initially, meticulous design and printing of 3D templates were conducted, as previously described. Subsequently, precise solutions comprising

resorcinol (R), formaldehyde (F), water (W), and the catalyst  $\text{Cs}_2\text{CO}_3$  (Cs) were prepared, maintaining specific molar ratios:  $\text{R/F} = 1/2$  and  $\text{R/W} = 1/15$ . To tailor the porosity of the resulting monoliths, the R/Cs ratio was systematically varied at 100, 500, 1000 and 2000. The solutions, along with the 3D printed templates, were poured into cylindrical glass molds and hermetically sealed, marking the commencement of the polymerization and curing process. Over the course of 1 day at ambient temperature, followed by 1 day at 50 °C, and concluding with 5 days at 80 °C, the polymerization and curing process was completed. Upon completion, the resulting organic polymer was demolded, sectioned to the desired dimensions, and submerged in a 2 M acetic acid solution for 1 day in order to stabilize the organic monolith. The water occupying the developed porosity was then displaced with acetone over a 3-day period, with solution changes performed twice daily. This resulted in the formation of organic monoliths with the 3D-printed template seamlessly integrated within the organic gel matrix. The organic monoliths were air-dried at room temperature before being carbonized in a  $\text{N}_2$  flow of 150 mL/min. The carbonizing process involved a preliminary treatment at 300 °C for two hours to stabilize the monolith, followed by a second heating phase at 850 °C for a further two hours. In both cases, the heating rate was 1.5 °C/min. Throughout the first carbonization process, the 3D-printed template was removed, leaving behind intricate channel morphologies within the resulting carbon monoliths. The final dimensions of the manufactured 3D-printed carbon monoliths were 1.4 cm in diameter and 2.3 cm in length. These monoliths were designated as Monolith-100, Monolith-500, Monolith-1000 and Monolith-2000, in accordance with the variations in the R/Cs ratio during fabrication. Additionally, carbon monoliths synthesized without utilizing 3D printing technology were also produced as a reference set, named as Reference-100, Reference-500, Reference-1000 and Reference-2000.

### **10.2.3 Characterization of 3D-printed carbon monoliths**

The morphology of the 3D-printed carbon monoliths was obtained by scanning electron microscopy with a FEI microscope, model Quanta 400 (Hillsboro, Oregon, USA). This technique was employed to analyze both the channel geometries and the

carbon mass morphologies. The textural properties of the 3D-printed carbon monoliths were accurately characterized through the acquisition of  $N_2$  and  $CO_2$  adsorption isotherms at  $-196.15$  and  $0$   $^{\circ}C$ , respectively, utilizing an Autosorb-6B from Quantachrome (Boynton Beach, Florida, USA). Additionally, Hg intrusion porosimetry curves were acquired using an AutoPore V Micromeritics Hg porosimeter (Norcross, Georgia, USA). The textural properties of the monoliths were calculated using the procedure outlined in Section 9.2.2.



**Figure 10.1.** CAD 3D templates of interconnected network channels (a) and straight channels (b), with side, top and bottom views.

The point of zero charge ( $pH_{PZC}$ ) of the 3D-printed carbon monoliths was determined using a variant proposed by Leon and Leon et al. (1992), based on the approach developed by Noh and Schwarz (1989). In this method, 4 mL of  $CO_2$ -free distilled water were added to a volumetric flask containing 0.25 g of the monolith. The suspension was then placed in a water thermostatic bath at  $25$   $^{\circ}C$  with continuous agitation. The pH of the solution was measured periodically until it stabilized, and the final pH value was considered as the  $pH_{PZC}$ .

The concentration of acidic and basic sites in the 3D-printed carbon monoliths were estimated using the titration method developed by Boehm (1966), as detailed in Section 9.9.2.

#### 10.2.4 Adsorbate and quantification

Sulfamethoxazole (SMX) (CAS: 723-46-6) was sourced by Merck, with the key physicochemical properties detailed in Table 9.1. In aqueous environments, SMX demonstrates different ionic states depending on the solution pH. When the pH is below 1.6, SMX is predominantly cationic. Between pH 1.6 and 5.7, the neutral chemical species is the dominant form, while at pH values exceeding 5.7, the negative form is the prevailing species.

The concentrations of SMX in water solutions were quantified using a Shimadzu UV-Vis spectrophotometer, model 2600i, configured at 264 nm. The absorbance readings were recorded, and calibration curves were established using concentrations ranging from 1 to 20 mg/L to determine the concentrations of SMX.

#### 10.2.5 Experimental data of adsorption equilibrium

The adsorption capacities of the 3D-printed carbon monoliths for SMX were determined in a batch system using the following procedure. Initially, solutions of SMX with concentrations ranging from 25 to 200 mg/L were prepared in 50 mL volumetric flasks and adjusted with NaOH 0.01 N and HCl 0.01 N electrolyte solutions. Simultaneously, representative pieces of each monolith were cut and placed in batch adsorbers, containing 40 mL of each prepared SMX solution. These dispersions were then placed in a thermostatic water bath at 25 °C with continuous vigorous stirring. The pH of the solution was adjusted daily and maintained at a value of 7 using drops of NaOH 0.01 N or HCl 0.01 N solutions. Adsorption equilibrium was considered achieved when the concentrations of two consecutive samples remained constant over time, indicating equilibrium within 4 days. After 5 days, samples from each adsorber were filtered, and the concentrations of SMX at the beginning and end of the adsorption experiment were quantified as previously described. The uptake of SMX adsorbed on each monolith was calculated with the mass balance equation described above:

$$q = \frac{V}{m}(C_o - C_e) \quad (10.1)$$

where  $C_e$  and  $C_o$  are the SMX equilibrium and initial concentrations, mg/L;  $m$  is the mass of the 3D-printed carbon monolith, g;  $q$  is the uptake of SMX adsorbed on the 3D-printed carbon monolith, mg/g;  $V$  is the volume of the solution, L.

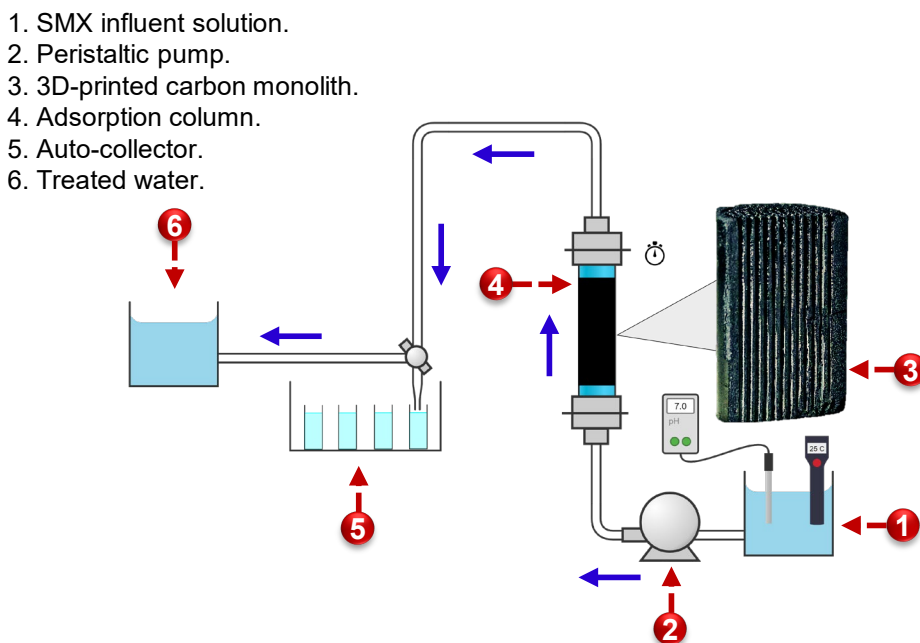
#### **10.2.6 Experimental data of breakthrough curves**

Breakthrough curves for SMX adsorption on the 3D-printed carbon monoliths were measured in a monolithic packed bed adsorber, comprising an acrylic column (10 cm height and 1.5 cm inner diameter) connected to a peristaltic pump at the column entrance and a sample auto-collector at the exit (Figure 10.2). The assembly of the monolithic adsorption column followed the next procedure. First, the column was packed with glass beads to a height of 3 cm to ensure homogeneous distribution of the solution before entering the monolith. Subsequently, a 3D-printed carbon monolith was inserted into the column, and glass beads were added to completely fill the acrylic column. The bottom entrance of the column was connected to a peristaltic pump for feeding the solution, while the upper exit was connected to a sample auto-collector and then to a 2 L container for collecting the effluent solution.

Experimental data collection began with the introduction of contaminant-free distilled water to the monolithic bed for 24 h to eliminate trapped air in the packed bed. After the preconditioning period, a solution of SMX (initial concentration,  $C_{A0} = 50$  mg/L) was fed to the packed bed at a specific volumetric flow rate. The chronometer was initiated upon contact of the solution with the 3D-printed carbon monolith. Effluent samples were collected at various time intervals using the auto collector, and the concentration of the solutions was quantified using the spectrophotometric method described above. The experiment ended when the concentration in the effluent equaled that of the influent.

Breakthrough curves were constructed by plotting the concentration of SMX against time per unit mass of monolith, with the R/Cs ratio, volumetric flow rate and channel geometry serving as the operating variables.





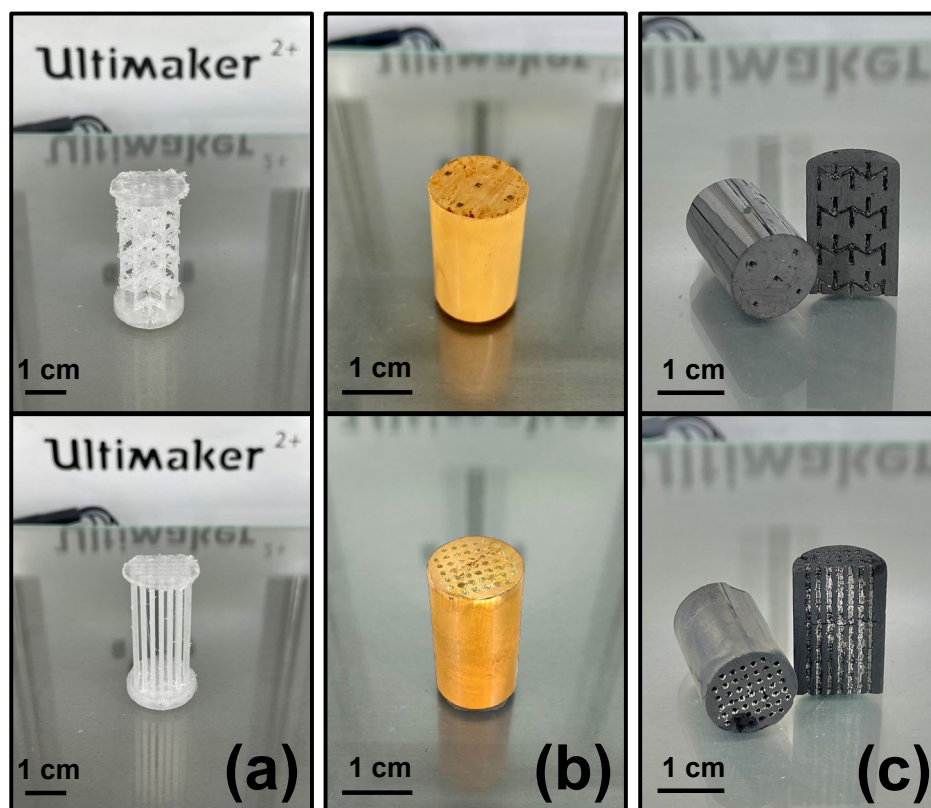
**Figure 10.2.** Monolithic packed-bed adsorber.

### 10.3 Results and discussion

#### 10.3.1 Fabrication of 3D-printed carbon monoliths

Figure 10.3 illustrates the step-by-step process involved in fabricating the 3D-printed carbon monoliths, showing two different channel geometries: interconnected network channels and straight channels. Figure 10.3 (a) shows meticulously designed 3D-printed polymer templates, exhibiting flawless replication of the original CAD 3D templates (see Figure 10.1). Moving to Figure 10.3 (b), views of the organic monoliths post-polymerization and curing are presented. Notably, regardless of the channel architecture, the polymeric templates seamlessly integrate within the organic gel matrix, with no discernible presence of gaps within the walls or at the interface between the organic gel and the 3D printed template. This observation highlights the strong adhesion and compatibility between the polymeric template and the organic gel, ensuring precise control, optimal integration and structural integrity of the final monolithic structures. Figure 10.3 (c) shows the final 3D-printed carbon monoliths, demonstrating that the polymer template has been successfully removed after

carbonization, leaving behind impeccably conforming channel morphologies within the integral carbon bulk, as originally designed by 3D printing. Notably, in the interconnected network channel configuration, the channels formed a complex labyrinth with pathways crossing both vertically and horizontally. This complex network facilitates the existence of multiple pathways for fluid flow, thereby enhancing mass transfer within the monolithic structure. Conversely, in the straight channel configuration, the channels presented a conventional linear pattern, providing a more direct and straightforward path for fluid flow. These results demonstrate the capability of 3D printing technology to perfectly control the configuration of sophisticated channel geometries within the monoliths, highlighting its precision and versatility in materializing intricate designs.



**Figure 10.3.** Illustration showing CAD 3D printed templates (a), organic monoliths after polymerization and curing process (b) and final 3D-printed carbon monolith adsorbents cross section showing channel geometries (c).

Table 10.1 presents the main characteristics of the fabricated 3D-printed carbon monoliths. Both configuration of channels maintains a similar total volume, with dimensions of 1.4 cm in diameter and 2.3 cm in length. However, there is a disparity in the volume of channels between the two designs, attributable to their different channel geometries. Furthermore, the channel width in all fabricated monoliths remain constant at 0.7 mm. In the monolith configured with straight channels, the volume of channels is 2.2-fold higher than in the monolith configured with interconnected network channels. Consequently, this variance in channel volume results in differences in the volume of the solid, with the monolith featuring interconnected network channels having a greater volume of solid material than the monolith with straight channels.

**Table 10.1.** Characteristics of the fabricated 3D-printed carbon monolith adsorbents.

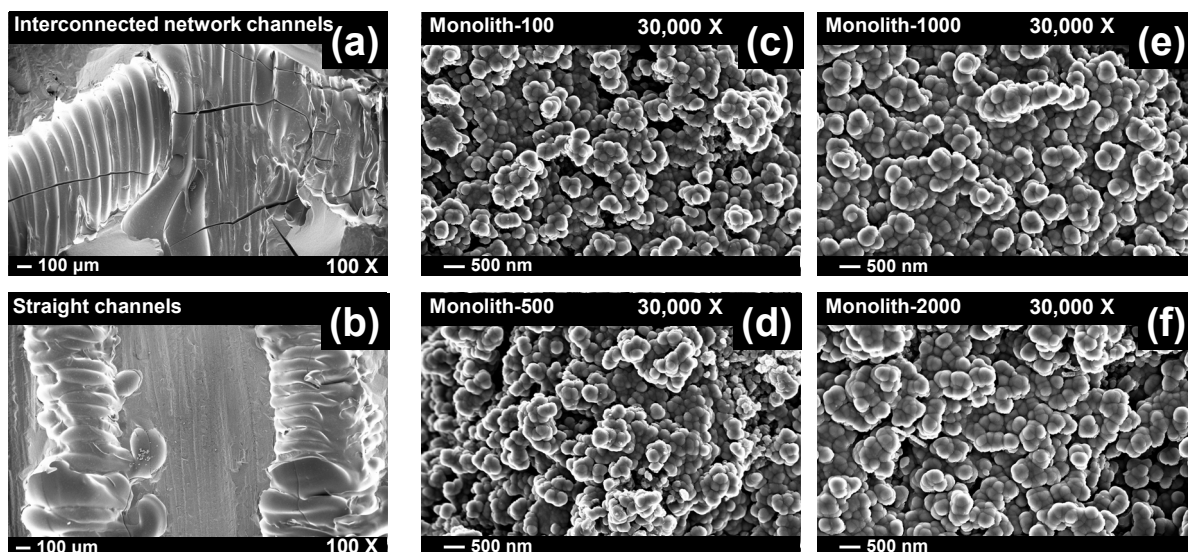
| Channel geometry                | Total volume of the monolith (cm <sup>3</sup> ) | Volume of channels (cm <sup>3</sup> ) | Volume of the solid (cm <sup>3</sup> ) | Channel width (mm) |
|---------------------------------|-------------------------------------------------|---------------------------------------|----------------------------------------|--------------------|
| Interconnected network channels | 3.541                                           | 0.231                                 | 3.310                                  | 0.7                |
| Straight channels               | 3.541                                           | 0.516                                 | 3.025                                  | 0.7                |

### 10.3.2 Characterization of 3D-printed carbon monoliths

Figure 10.4 shows SEM images capturing the CAD-designed channel geometries of the 3D-printed carbon monoliths, including both designs, along with their bulk carbon morphology with variations in the R/Cs ratio. In Figures 10.4 (a) and 10.4 (b), the fidelity of channel morphology replication via 3D printing technology is evident in both channel geometries, regardless of the R/Cs ratio. Surface irregularities observed on the channel surfaces and in the channel-carbon interphase bulk are attributed to the layer-by-layer deposition printing process. These irregularities emphasize the potential utility of 3D printing technology for achieving precise replicas at the micrometric scale.

In Figures 10.4 (c) to 10.4 (f), a series of images depicts the carbon bulk of the 3D-printed carbon monoliths at varying R/Cs ratios. These images reveal the significant

influence of synthesis conditions on carbon morphology. Across these figures, spherical primary particles interconnected to form a three-dimensional network or skeleton are evident in all samples. As the R/Cs ratio increases, noticeable differences in the size of these spherical particles become apparent. For instance, in the Monolith-2000 sample (Figure 10.4 (f)) which has the lowest catalyst concentration, fewer nucleation centers are generated, which facilitates the formation of larger particles and interparticle sizes within the skeleton structure. Conversely, in the Monolith-100 sample (Figure 10.4 (c)), the higher catalyst concentration results in the formation of a greater number of nucleation centers, resulting in smaller particle sizes and reduced interparticle sizes within the skeleton compared to the Monolith-2000 sample. Meanwhile, the Monolith-500 (Figure 10.4 (d)) and Monolith-1000 (Figure 10.4 (e)) samples exhibit a diverse range of primary particle sizes, falling within the range observed between the extremes registered in the Monolith-100 and Monolith-2000 samples.



**Figure 10.4.** SEM images depicting the interconnected network (a) and straight (b) channel geometries, with detailed views of the carbon bulk morphology at various R/Cs ratios (c-f).

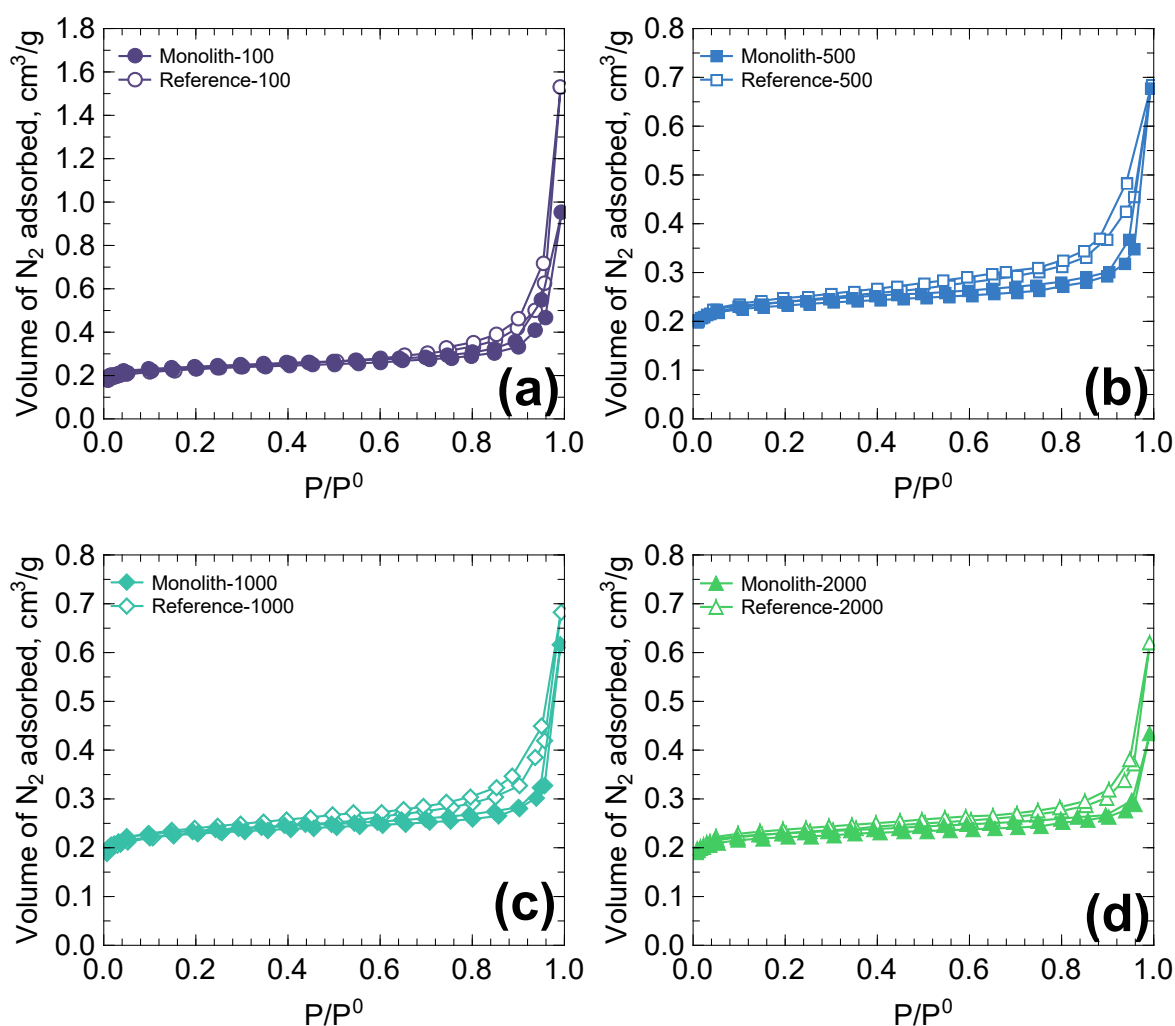
Figure 10.5 presents the N<sub>2</sub> adsorption-desorption isotherms at -196.15 °C of the monoliths. For comparison, the adsorption-desorption isotherms for the reference samples, synthesized without the use of a 3D printed template, were also analyzed. The textural properties of the monoliths are summarized in Table 10.2. Overall, these isotherms show a combined category of type Ia and IIb isotherms, as per the IUPAC classification, indicating hierarchical porosity in the carbon monoliths (Rouquerol et al., 1998; Thommes et al., 2015). Type IIb, characterized by an absence of a plateau at high  $P/P^0$  values, is associated with meso- and macropores formed by the voids between interconnected spherical primary particles observed in SEM images, while type Ia corresponds to micropores within these particles. Narrow hysteresis loops suggest wide pores primarily fall within the range of macropores (> 50 nm), regardless of the R/Cs ratio. Furthermore, no significant differences were observed in the adsorption isotherms with varying R/Cs ratios, indicating the primary influence of this ratio on macropore sizes and thus, the skeleton size.

Comparison with corresponding reference isotherms revealed minimal reductions in the volume of N<sub>2</sub> adsorbed for  $P/P^0$  values above 0.5, suggesting minimal blockage of porosity due to the utilization of a 3D-printed template in the synthesis process. The slight obstruction of porosity can be attributed to carbon deposition from the polymer template during the carbonization step (Parra-Marfil et al., 2024). Notably, when observing the  $S_{\text{BET}}$  and  $V_{\text{mic}}(\text{N}_2)$  values of the carbon monoliths (see Table 10.2), they remained similar when compared to their respective reference samples, suggesting that while microporosity remains unaffected by using a 3D-printed template, macroporosity is slightly obstructed.

The Hg porosimetry curves in Figure 10.6 (a) show significant differences in the volume of Hg intruded into the carbon monoliths compared to their references at different R/Cs ratios. Regardless of the R/Cs ratio, there is a consistent reduction in the volume of Hg intruded at pressures above 20 MPa for all samples, albeit this reduction becomes less pronounced as the R/Cs ratio increases.

This phenomenon has an impact on the  $V_p$  and  $S_{\text{ext}}(\text{Hg})$  values (Table 10.3). For instance, in the Monolith-100 sample,  $V_p$  diminishes by 35.1 % and  $S_{\text{ext}}(\text{Hg})$  decreases

by 58.7 % compared to its reference, whereas these reductions are milder at 12.5 % for  $V_p$  and 29.8 % for  $S_{ext}(Hg)$  in the Monolith-2000 sample. These findings support the notion that the utilization of a 3D printed template obstructs the macroporosity of the resulting 3D-printed carbon monoliths. This effect is less pronounced as the R/Cs ratio increases. Although the alteration in the textural properties of the fabricated 3D-printed monoliths is not significant compared to all advantages that 3D printing technology offers, it should be considered when designing and manufacturing these new 3D-printed carbon monolith adsorbents.



**Figure 10.5.**  $N_2$  adsorption-desorption isotherms on carbon monoliths at  $-196.15\text{ }^\circ\text{C}$  for varying R/Cs ratios: 100 (a), 500 (b), 1000 (c) and 2000 (d).

**Table 10.2.** Textural properties of the 3D-printed carbon monoliths obtained by N<sub>2</sub> and CO<sub>2</sub> adsorption data and their corresponding reference samples.

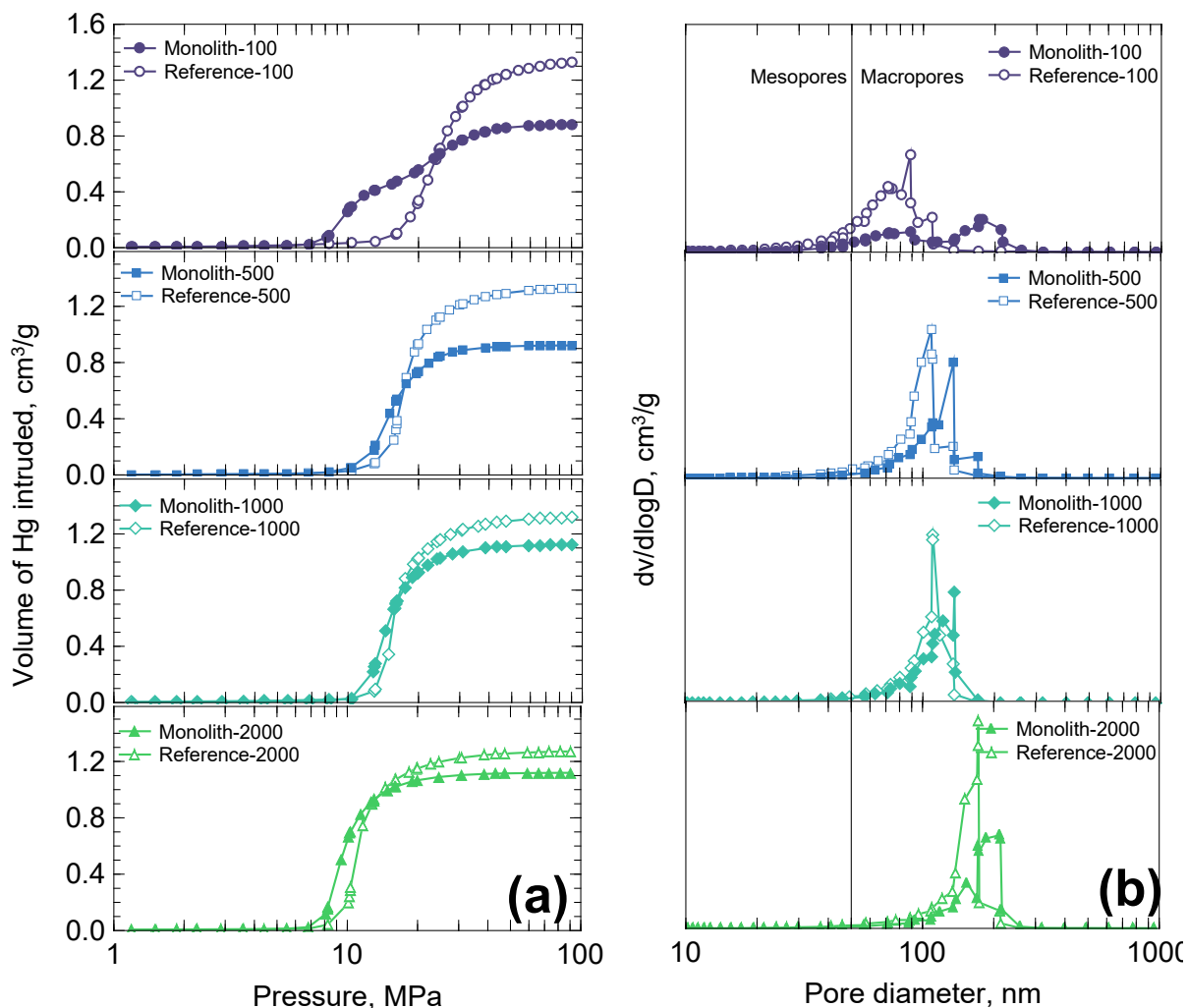
| Monoliths      | N <sub>2</sub> isotherm                 |                                          |                                                            |                                                           | CO <sub>2</sub> isotherm                  |                                                             | Hg porosimetry                         |                        |
|----------------|-----------------------------------------|------------------------------------------|------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------|----------------------------------------|------------------------|
|                | S <sub>BET</sub><br>(m <sup>2</sup> /g) | L <sub>0</sub> (N <sub>2</sub> )<br>(nm) | V <sub>mic</sub> (N <sub>2</sub> )<br>(cm <sup>3</sup> /g) | S <sub>mic</sub> (N <sub>2</sub> )<br>(m <sup>2</sup> /g) | L <sub>0</sub> (CO <sub>2</sub> )<br>(nm) | V <sub>mic</sub> (CO <sub>2</sub> )<br>(cm <sup>3</sup> /g) | V <sub>p</sub><br>(cm <sup>3</sup> /g) | D <sub>p</sub><br>(nm) |
| Monolith-100   | 556                                     | 1.07                                     | 0.227                                                      | 426                                                       | 0.57                                      | 0.255                                                       | 0.877                                  | 95.1                   |
| Reference-100  | 551                                     | 1.23                                     | 0.220                                                      | 360                                                       | 0.58                                      | 0.249                                                       | 1.352                                  | 60.4                   |
| Monolith-500   | 580                                     | 0.93                                     | 0.230                                                      | 496                                                       | 0.58                                      | 0.265                                                       | 0.920                                  | 102.5                  |
| Reference-500  | 587                                     | 1.13                                     | 0.234                                                      | 415                                                       | 0.57                                      | 0.248                                                       | 1.336                                  | 84.4                   |
| Monolith-1000  | 572                                     | 0.91                                     | 0.227                                                      | 499                                                       | 0.58                                      | 0.260                                                       | 1.104                                  | 131.4                  |
| Reference-1000 | 565                                     | 1.14                                     | 0.226                                                      | 397                                                       | 0.57                                      | 0.249                                                       | 1.322                                  | 90.7                   |
| Monolith-2000  | 571                                     | 0.98                                     | 0.222                                                      | 454                                                       | 0.57                                      | 0.263                                                       | 1.112                                  | 157.1                  |
| Reference-2000 | 573                                     | 1.02                                     | 0.228                                                      | 446                                                       | 0.60                                      | 0.269                                                       | 1.271                                  | 126.1                  |

Figure 10.6 (b) illustrates the Hg-pore size distribution curves (PSD) of the carbon monoliths at different R/Cs ratios, revealing the predominance of macropores in the monolithic structures. Moreover, notable variations are observed in the PSD curves as the R/Cs ratio is modified, with a shift towards higher pore diameters as the ratio increases. For instance, in the Monolith-100 sample, the resulting pore diameter was 95.1 nm (see Table 10.3), indicating narrower macropores, while in the Monolith-2000 sample, it increased to 157.1 nm, revealing wider macropores. The mean pore diameters for the Monolith-500 and Monolith-1000 samples were 102.5 and 131.4 nm, respectively, falling within the extremes. These changes in macropore diameters correspond to variations in the sizes of the spherical primary particles observed in SEM images, highlighting the adjustability of the skeleton macrostructure by varying the R/Cs ratio.

The results presented herein demonstrate the efficacy of sol-gel polymerization in the manufacture of 3D-printed carbon monoliths with diverse skeleton and pore sizes. The resulting monolithic structures exhibit highly accessible macroporosity and reduced flow resistance, making them ideal for liquid-phase adsorption applications.

Alterations in the shape of the PSD curves compared to their corresponding references result in a reduction in the area under the PSD curve and a slight shift to

higher pore diameters. These observations, as discussed earlier, are attributed to the slight blockage of porosity caused by the utilization of a 3D-printed template during fabrication.



**Figure 10.6.** Hg intrusion porosimetry curves of the carbon monoliths (a) and PSD curves obtained by Hg porosimetry data (b).

The CO<sub>2</sub> adsorption isotherms of the carbon monoliths and their reference counterparts are depicted in Figure 10.7. No differences in the volume of CO<sub>2</sub> adsorbed were observed when the R/Cs ratio was varied, demonstrating that microporosity is not affected by adjustments to this molar ratio. The micropores develop only inside the primary particles and their microporous structure is only conditioned by the synthesis



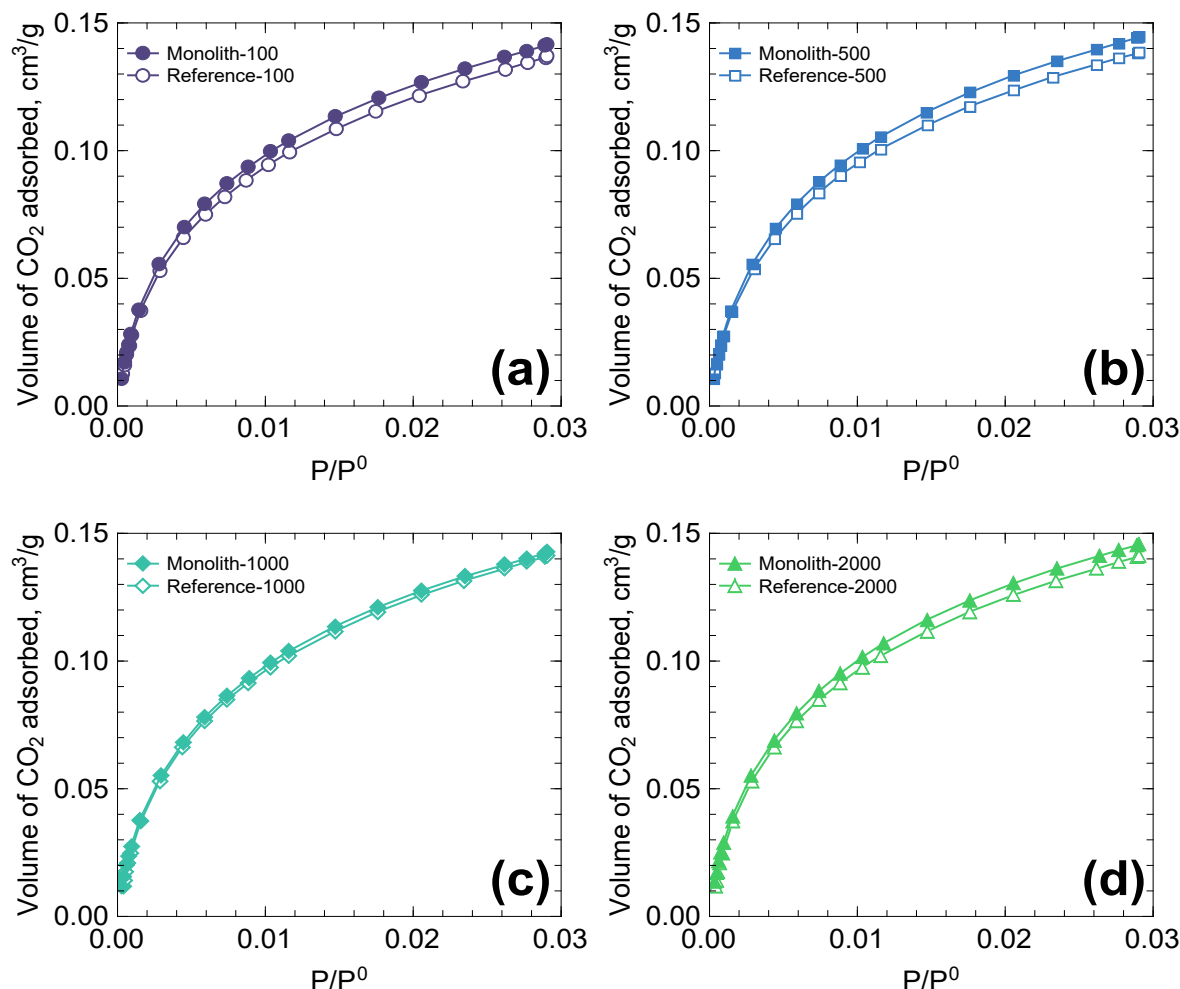
conditions, mainly the R/F ratio and the type of catalyst (Fairén-Jiménez et al., 2008). Furthermore, careful scrutiny revealed minimal variations in the isotherms compared to their reference samples, supporting the conclusion that microporosity remains unchanged despite the incorporation of a 3D-printed template during the synthesis process. The consistent values of the textural properties such as  $L_0(\text{CO}_2)$ ,  $L_0(\text{N}_2)$  and  $V_{\text{mic}}(\text{CO}_2)$  further reinforce the assertion that microporosity remains unaltered regardless of variations in the R/Cs ratio or the utilization of a 3D-printed template during fabrication.

**Table 10.3.** Textural properties of the 3D-printed carbon monoliths analyzed by Hg intrusion porosimetry and their corresponding reference samples.

| Monoliths      | Hg porosimetry                                             |                                                           |                                                             |                                                            |                                                          |
|----------------|------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|------------------------------------------------------------|----------------------------------------------------------|
|                | $V_{\text{meso}}(\text{Hg})$<br>( $\text{cm}^3/\text{g}$ ) | $S_{\text{meso}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) | $V_{\text{macro}}(\text{Hg})$<br>( $\text{cm}^3/\text{g}$ ) | $S_{\text{macro}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) | $S_{\text{ext}}(\text{Hg})$<br>( $\text{m}^2/\text{g}$ ) |
| Monolith-100   | 0.077                                                      | 8.2                                                       | 0.800                                                       | 28.7                                                       | 36.9                                                     |
| Reference-100  | 0.277                                                      | 34.5                                                      | 1.075                                                       | 55.0                                                       | 89.5                                                     |
| Monolith-500   | 0.035                                                      | 3.8                                                       | 0.885                                                       | 32.1                                                       | 35.9                                                     |
| Reference-500  | 0.091                                                      | 11.5                                                      | 1.245                                                       | 51.7                                                       | 63.3                                                     |
| Monolith-1000  | 0.021                                                      | 3.5                                                       | 1.083                                                       | 30.1                                                       | 33.6                                                     |
| Reference-1000 | 0.098                                                      | 11.7                                                      | 1.224                                                       | 46.6                                                       | 58.3                                                     |
| Monolith-2000  | 0.016                                                      | 1.6                                                       | 1.097                                                       | 26.7                                                       | 28.3                                                     |
| Reference-2000 | 0.048                                                      | 5.8                                                       | 1.223                                                       | 34.5                                                       | 40.3                                                     |

Table 10.4 presents the chemical properties of the 3D-printed carbon monoliths, including the total concentration of acidic and basic sites, as well as the  $\text{pH}_{\text{PZC}}$  values. Overall, the analysis reveals that the chemical nature of the carbon monoliths exhibits minimal variation with changes in the R/Cs ratio. Notably, all monolith samples consistently exhibit a predominance of basic characteristics, with a higher concentration of total basic sites compared to acidic sites in all samples. The  $\text{pH}_{\text{PZC}}$  values of the monoliths are observed to be approximately 8, indicating a transition from a positively charged surface at pH values below 8 to a negatively charged surface at pH values above 8. Interestingly, these  $\text{pH}_{\text{PZC}}$  values remain consistent irrespective of

the R/Cs ratio. This positive surface charge at pH values below 8 can promote the adsorption of negatively charged SMX molecules through electrostatic attractions between the molecules and the positively charged surface of the monoliths.



**Figure 10.7.** CO<sub>2</sub> adsorption isotherms on carbon monoliths at 0 °C for varying R/Cs ratios: 100 (a), 500 (b), 1000 (c) and 2000 (d).

### 10.3.3 Adsorption equilibrium isotherms

Information about adsorption equilibrium of SMX on 3D-printed carbon monoliths is essential for understanding the dynamic behavior within the monolithic adsorbents. Experimental data on adsorption equilibrium were obtained using a representative piece of the monolith, with variations in the R/Cs ratio. Additionally,

adsorption equilibrium data were collected for reference carbon monoliths fabricated without 3D printing technology.

**Table 10.4.** Concentration of acidic and basic sites and  $\text{pH}_{\text{PZC}}$  values of the 3D-printed carbon monoliths.

| Monoliths     | Total acidic sites<br>(meq/g) | Total basic sites<br>(meq/g) | $\text{pH}_{\text{PZC}}$ |
|---------------|-------------------------------|------------------------------|--------------------------|
| Monolith-100  | 0.39                          | 0.62                         | 8.3                      |
| Monolith-500  | 0.38                          | 0.60                         | 8.1                      |
| Monolith-1000 | 0.34                          | 0.61                         | 8.2                      |
| Monolith-2000 | 0.41                          | 0.61                         | 8.1                      |

The adsorption equilibrium data of SMX on the 3D-printed carbon monoliths from the aqueous solutions were interpreted by the Freundlich, Langmuir and Radke-Prausnitz isotherm models, described by the Equations (4.9-4.11).

Table 10.5 lists the estimated parameters and the average percentage deviation ( $\%D_{\text{ai}}$ ) of the adsorption isotherms of SMX on the 3D-printed carbon monoliths. The experimental data of adsorption equilibrium were best interpreted by the Freundlich isotherm model, as indicated by the low average percentage deviation in 7 out of 8 cases compared to those of Langmuir and Radke-Prausnitz isotherms. The average deviation percentage for each Freundlich isotherm was less than 6.3 %.

Figure 10.8 illustrates the adsorption isotherms of SMX on the 3D-printed carbon monoliths at  $\text{pH} = 7$  and  $T = 25\text{ }^{\circ}\text{C}$ . The results revealed high adsorption capacities of the 3D-printed carbon monoliths for SMX, although notable differences in adsorption capacity were observed concerning the R/Cs ratio and their respective references. Across all R/Cs ratios, a decrease in adsorption capacity compared to their references was evident, with these decreases becoming less pronounced as the R/Cs ratio increased. These reductions in adsorption capacity can be attributed to the slight obstruction of porosity by the 3D-printed template, as observed through Hg porosimetry. The reductions in total pore volume become less pronounced as the R/Cs

ratio increases, aligning with the observed reduction in adsorption capacity, which also lessens as the R/Cs ratio increases.

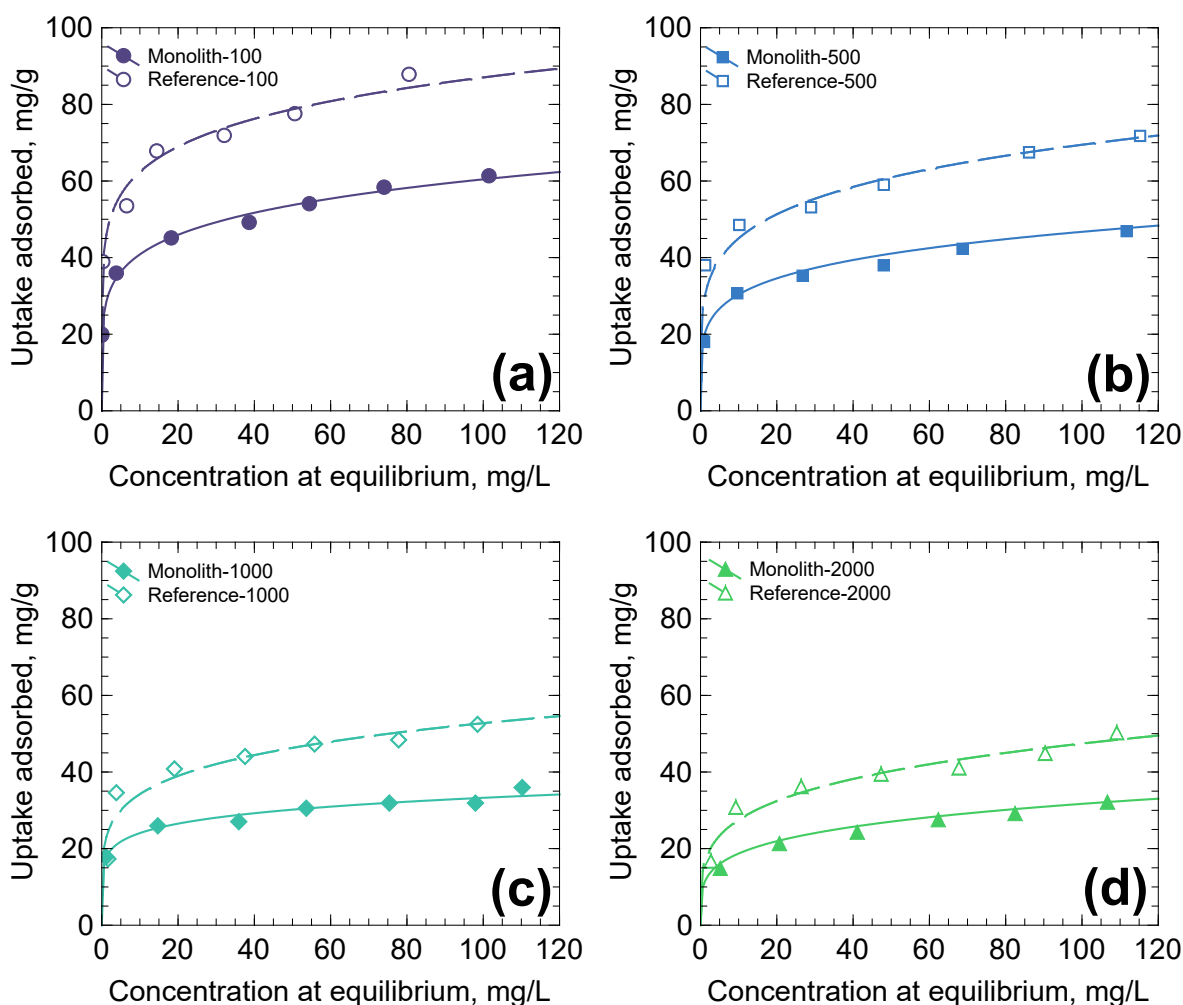
**Table 10.5.** Parameters and average percentage deviation of adsorption isotherms of SMX on carbon monoliths at pH = 7, I = 0.01 N and T = 25 °C.

| Sample         | Langmuir        |             |                  | Freundlich                                         |       |                  | Radke-Prausnitz |                                         |      |                  |
|----------------|-----------------|-------------|------------------|----------------------------------------------------|-------|------------------|-----------------|-----------------------------------------|------|------------------|
|                | $q_m$<br>(mg/g) | K<br>(L/mg) | %D <sub>ai</sub> | $K_F$<br>(mg <sup>1-1/n</sup> L <sup>1/n</sup> /g) | $n_F$ | %D <sub>ai</sub> | a<br>(L/g)      | b<br>(L <sup>β</sup> /mg <sup>β</sup> ) | β    | %D <sub>ai</sub> |
| Monolith-100   | 52.15           | 2.869       | 15.1             | 27.59                                              | 5.9   | 1.7              | 960.8           | 35.846                                  | 0.82 | 4.1              |
| Reference-100  | 72.94           | 4.657       | 11.2             | 44.70                                              | 6.9   | 4.8              | 488.7           | 9.782                                   | 0.88 | 7.8              |
| Monolith-500   | 42.48           | 1.252       | 14.3             | 19.74                                              | 5.3   | 4.4              | 413.3           | 19.999                                  | 0.81 | 4.9              |
| Reference-500  | 63.33           | 0.771       | 13.8             | 29.19                                              | 5.3   | 6.3              | 232.2           | 7.126                                   | 0.84 | 6.9              |
| Monolith-1000  | 31.28           | 1.172       | 7.4              | 17.39                                              | 7.1   | 3.0              | 125.7           | 6.540                                   | 0.88 | 3.5              |
| Reference-1000 | 25.57           | 1.403       | 5.2              | 22.20                                              | 5.3   | 4.6              | 861.2           | 38.178                                  | 0.82 | 4.6              |
| Monolith-2000  | 33.04           | 0.121       | 9.1              | 11.06                                              | 4.4   | 4.2              | 80.53           | 8.348                                   | 0.74 | 2.7              |
| Reference-2000 | 33.43           | 0.949       | 9.6              | 15.96                                              | 4.2   | 5.1              | 382.6           | 23.697                                  | 0.77 | 5.1              |

Figure 10.9 shows the effect of the R/Cs ratio on the adsorption capacity of the 3D-printed carbon monoliths for SMX. It is evident that reducing the R/Cs ratio enhances the adsorption capacity. The maximum adsorption capacity was observed in the Monolith-100 sample (61.4 mg/g), followed by Monolith-500, Monolith-1000 and Monolith-2000 in decreasing order. Specifically, the maximum adsorption capacities in the Monolith-500, Monolith-1000 and Monolith-2000 samples were 52.7, 35.9 and 35.1 mg/g, respectively. This indicates that the adsorption capacity increases approximately 1.75 times when the R/Cs ratio is reduced from 2000 to 100. It was noted that the adsorption capacity increased as the  $S_{ext}(Hg)$  values rose (Table 10.3), indicating that adsorption primarily occurs in macropores and wide mesopores.

Two primary adsorption mechanisms can contribute to this phenomenon: first,  $\pi$ - $\pi$  dispersive interactions between the  $\pi$ -acceptors present in the functional amino group and N-heteroaromatic ring of SMX, and the  $\pi$ -donors within the carbon monoliths; second, electrostatic attractions between the positively charged surface of the carbon monoliths at pH = 7 and the negatively charged molecules of SMX. These mechanisms collectively enhance the adsorption capacity of the carbon monoliths,

particularly as the R/Cs ratio decreases, highlighting the significance of synthesis conditions in tailoring adsorption properties of 3D-printed carbon monoliths for effective SMX removal. Similar adsorption mechanisms for the removal of pharmaceutical compounds on carbon gel-based adsorbents have been reported by several authors (Carrales-Alvarado et al., 2022; Segovia-Sandoval et al., 2020).

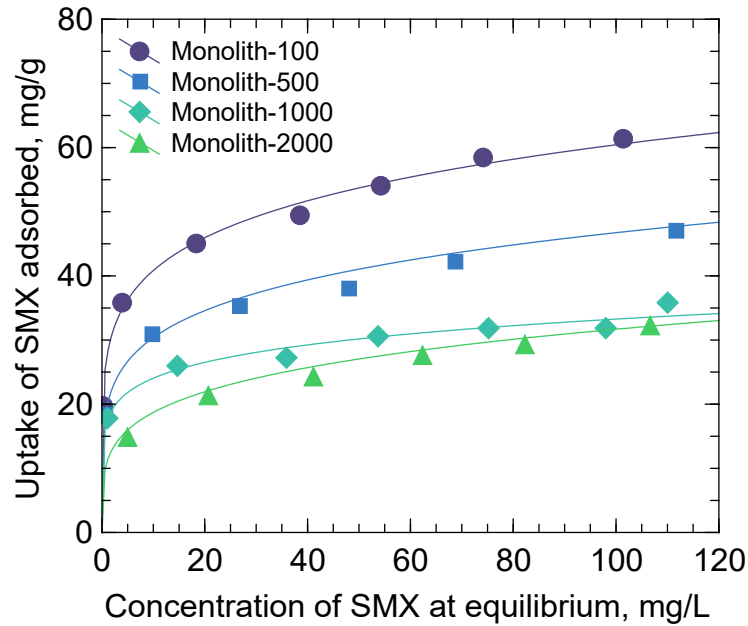


**Figure 10.8.** Adsorption isotherms of SMX on carbon monoliths at pH = 7 and T = 25 °C for varying R/Cs ratios: 100 (a), 500 (b), 1000 (c) and 2000 (d). The lines represent the Freundlich isotherm.

### 10.3.4 Dynamic breakthrough curves

The dynamic adsorption performance of SMX on 3D-printed carbon monoliths was investigated using breakthrough curves obtained from a monolithic packed bed

adsorber. Operational parameters such as the R/Cs ratio, volumetric flow rate and channel geometry were varied to assess the efficiency of the monolithic column for scale-up applications. Several key parameters, including adsorption capacity, breakthrough time, treated volume, mass transfer zone and mass transfer zone displacement rate, were analyzed to characterize the dynamic adsorption process.



**Figure 10.9.** Effect of the R/Cs ratio on SMX adsorption isotherms on the 3D-printed carbon monoliths at pH = 7 and T = 25 °C. The lines represent the Freundlich isotherm.

To quantify the uptake of SMX adsorbed at both the breakthrough time ( $t_b$ ) and saturation time ( $t_s$ ), the breakthrough point was defined at  $C_A/C_{A0} = 0.05$ , and the saturation point at  $C_A/C_{A0} = 0.95$ . The following equations were utilized to estimate the uptakes of SMX adsorbed:

$$q_b = \frac{QC_{A0}}{1000 \times m} \int_0^{t_b} \left(1 - \frac{C_A}{C_{A0}}\right) dt \quad (10.3)$$

$$q_s = \frac{QC_{A0}}{1000 \times m} \int_0^{t_s} \left(1 - \frac{C_A}{C_{A0}}\right) dt \quad (10.4)$$

where  $q_b$  is the uptake of SMX adsorbed at breakthrough time, mg/g;  $q_s$  is the uptake of SMX adsorbed at saturation time, mg/g;  $C_A$  is the concentration of SMX in the effluent, mg/L.

The mass transfer zone (MTZ) was defined as the region within the bed where the adsorption process occurs. As adsorption progresses, the MTZ moves forward, leading to the calculation of the mass transfer zone displacement rate. The length of the MTZ and its displacement rate were determined using the following equations:

$$H_{MTZ} = L \left( 1 - \frac{t_b}{t_s} \right) \quad (10.5)$$

$$R_{MTZ} = \frac{H_{MTZ} Q \times 60}{V_s - V_b} \quad (10.6)$$

where  $H_{MTZ}$  is the length of the mass transfer zone, cm;  $R_{MTZ}$  represents the rate of displacement of the MTZ, cm/h;  $L$  is the length of the 3D-printed carbon monolith, cm;  $V_s$  is the treated volume at saturation time, mL;  $V_b$  is the treated volume at breakthrough time, mL.

Figures 10.10 (a) and 10.10 (b) display the dynamic breakthrough curves illustrating SMX adsorption on 3D-printed carbon monoliths configured with interconnected network channels. These curves highlight the impact of the  $R/C_s$  ratio and volumetric flow rate on the adsorption process.

The experimental data were quite-well interpreted by the Bohart, Adams and Hutchins (BDST) empirical model describing the breakthrough performance. This model is represented by the following equation:

$$\frac{C_A}{C_{A0}} = \frac{e^{kC_{A0}t}}{e^{kC_{A0}t} + e^{\frac{kN_0L}{U}} - 1} \quad (10.7)$$

where:

$$U = \frac{Q}{A_T} \quad (10.8)$$

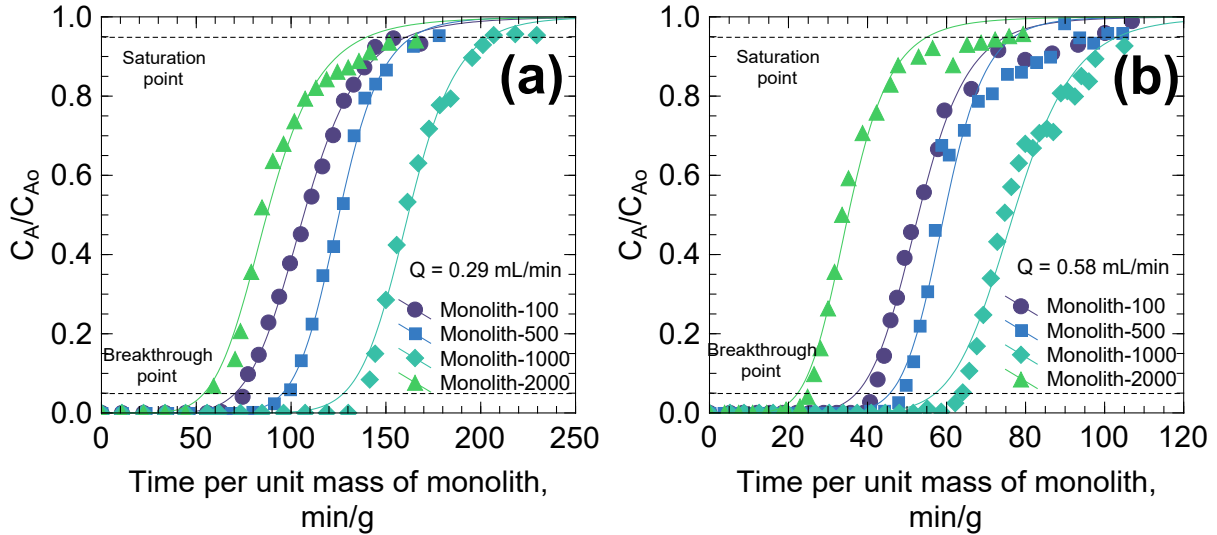
where  $k$  represents the BDST rate constant, L/min mg;  $N_0$  is the adsorption capacity per unit volume of fixed-bed, mg/L;  $U$  is the superficial velocity, cm/min;  $A_T$  represents the transversal area of the monolith, cm<sup>2</sup>. The best-fit parameter of each breakthrough

curve, alongside the average deviation percentage, were calculated through nonlinear fitting of the experimental data, using the following relationships:

$$\text{Objective relationship} = \sum_{i=1}^N \sqrt{\frac{((C_A/C_{A0})_{\text{exp}} - (C_A/C_{A0})_{\text{pred}})^2}{N - 2}} \quad (10.9)$$

$$\%D_{\text{BC}} = \left( \frac{1}{N} \sum_{i=1}^N \left| \frac{(C_A/C_{A0})_{\text{exp}} - (C_A/C_{A0})_{\text{pred}}}{(C_A/C_{A0})_{\text{exp}}} \right| \right) \times 100 \% \quad (10.10)$$

where  $N$  is the number of experimental data points;  $\%D_{\text{BC}}$  is average percentage deviation of the BDST model, %.



**Figure 10.10.** Effect of the R/Cs ratio on dynamic breakthrough curves for SMX adsorption on the 3D-printed carbon monoliths configured with interconnected network channels at  $C_{A0} = 50$  mg/L, pH = 7 and  $T = 25$  °C, for volumetric flow rates of 0.29 mL/min (a) and 0.58 mL/min (b). The lines represent the BDST model.

The estimated parameters of the BDST model and the average percentage deviation of the breakthrough curves for SMX adsorption on the 3D-printed carbon monoliths are listed in Table 10.6. The experimental data were adequately fitted by the BDST model since the average percentage deviation were less than 13 % for all experiments.



**Table 10.6.** Parameters of breakthrough curve experiments for SMX adsorption on 3D-printed carbon monoliths at  $C_{A0} = 50$  mg/L, pH = 7 and T = 25 °C.

| Exp. No. | R/Cs ratio | Q (mL/min) | Channel geometry       | $k \times 10^4$ (L/min mg) | $N_o$ (mg/L) | %D <sub>BC</sub> | $t_b$ (min) | $t_s$ (min) | $q_b$ (mg/g) | $q_s$ (mg/g) | $V_b$ (mL) | $V_s$ (mL) | H <sub>MTZ</sub> (cm) | R <sub>MTZ</sub> (cm/h) |
|----------|------------|------------|------------------------|----------------------------|--------------|------------------|-------------|-------------|--------------|--------------|------------|------------|-----------------------|-------------------------|
| 1        | 100        | 0.29       | Interconnected network | 8.7                        | 647.5        | 3.9              | 106         | 220         | 1.02         | 1.15         | 30.7       | 63.8       | 1.19                  | 0.627                   |
| 2        | 100        | 0.58       |                        | 25.2                       | 633.1        | 10.4             | 63          | 138         | 1.02         | 1.06         | 36.3       | 79.8       | 1.25                  | 1.004                   |
| 3        | 500        | 0.29       |                        | 12.4                       | 766.3        | 11.8             | 142         | 254         | 1.32         | 1.36         | 41.0       | 73.5       | 1.02                  | 0.544                   |
| 4        | 500        | 0.58       |                        | 27.6                       | 675.4        | 12.1             | 68          | 138         | 1.27         | 1.30         | 39.4       | 80.0       | 1.17                  | 1.000                   |
| 5        | 1000       | 0.29       |                        | 10.7                       | 952.9        | 7.3              | 200         | 292         | 1.70         | 1.74         | 57.9       | 84.5       | 0.73                  | 0.473                   |
| 6        | 1000       | 0.58       |                        | 19.5                       | 911.1        | 12.4             | 90          | 148         | 1.59         | 1.64         | 52.2       | 85.6       | 0.90                  | 0.936                   |
| 7        | 2000       | 0.29       |                        | 9.9                        | 499.6        | 8.0              | 84          | 234         | 0.77         | 0.91         | 24.2       | 67.7       | 1.48                  | 0.591                   |
| 8        | 2000       | 0.58       | Straight               | 37.1                       | 399.1        | 12.9             | 35          | 108         | 0.66         | 0.75         | 20.3       | 62.4       | 1.55                  | 1.284                   |
| 9        | 1000       | 0.58       |                        | 31.7                       | 121.8        | 4.6              | 5           | 115         | 0.09         | 0.26         | 2.9        | 66.7       | 2.20                  | 1.200                   |

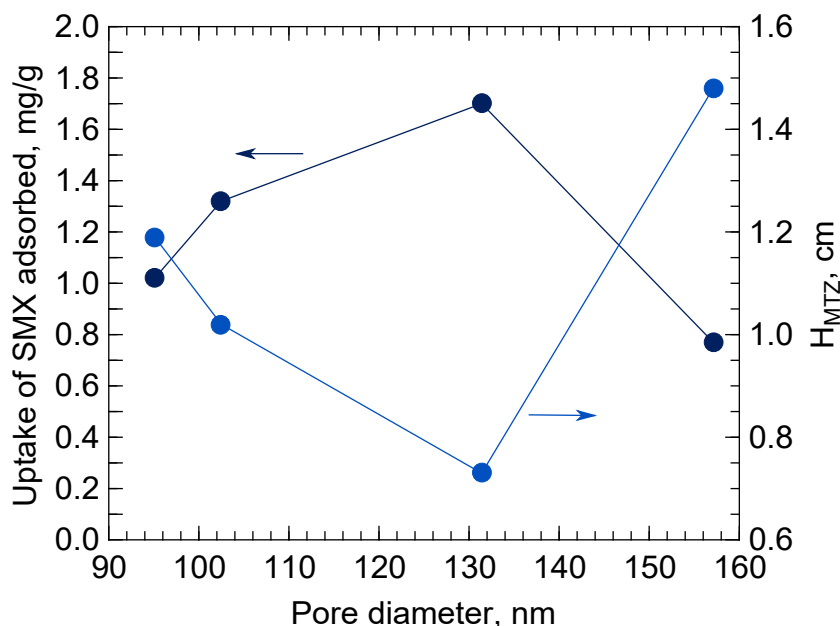
Analysis of the breakthrough curves, along with parameters listed in Table 10.6, reveals their sigmoidal shape, indicating favorable adsorption within the carbon monolithic structure. Variations in breakthrough times, influenced by the R/Cs ratio and flow rate, reveal the significance of synthesis conditions and operational variables on dynamic adsorption performance. At a volumetric flow rate of 0.29 mL/min (Figure 10.10 (a)), breakthrough times for Monolith-100, Monolith-500, Monolith-1000 and Monolith-2000 were 106, 142, 200 and 84 min, respectively. Interestingly, breakthrough times increased with R/Cs ratio from 100 to 1000 but decreased when increasing the ratio from 1000 to 2000. Analysis of adsorption capacities at the breakthrough point reveals that the Monolith-1000 exhibited the highest adsorption capacity at 1.70 mg/g, with the order decreasing as follows: Monolith-1000 > Monolith-500 > Monolith-100 > Monolith-2000. For a volumetric flow rate of 0.58 mL/min (Figure 10.10 (b)), the order of breakthrough times mirrored that of the 0.29 mL/min feed rate. Consequently, adsorption capacities followed the same trend as observed for the 0.29 mL/min feed rate. The H<sub>MTZ</sub> and R<sub>MTZ</sub> values, detailed in Table 10.6, emphasize the importance of short MTZ length and low velocity of MTZ for maximizing adsorber performance. Notably, Monolith-1000 exhibited the shortest H<sub>MTZ</sub> at 0.73 cm for 0.29 mL/min and 0.90 cm for 0.58 mL/min, with corresponding R<sub>MTZ</sub> values of 0.473 cm/h and 0.936 cm/h, respectively.

The observed differences between dynamic and batch adsorption experiments highlight the nuanced nature of adsorption behavior. In batch experiments, adsorption capacity decreased in the order: Monolith-100 > Monolith-500 > Monolith-1000 > Monolith-2000. However, dynamic adsorption showed a different trend: Monolith-1000 > Monolith-500 > Monolith-100 > Monolith-2000. This discrepancy suggests that dynamic adsorption is influenced not only by the increase in  $S_{\text{ext}}(\text{Hg})$  values. Instead, the accessibility of macroporosity, characterized by pore diameter size, emerges as a critical factor in dynamic adsorption operations. For effective dynamic adsorption, the porosity must be sufficiently wide to reduce flow resistance, allowing SMX molecules to access active sites as they traverse the monolith channels.

Figure 10.11 illustrates the variation of the uptake of SMX adsorbed at the breakthrough point and the mass transfer zone length as a function of the pore diameter values. Considering the results from Hg porosimetry, as the R/Cs ratio increases, the pore diameter or the size of the skeleton macrostructure also increases. The figure reveals that increasing the pore diameter to 131.4 nm resulted in an increase in adsorption capacity, regardless of the decrease in  $S_{\text{ext}}(\text{Hg})$  values (See Table 10.3). This phenomenon is attributed to the narrow pore diameter in the Monolith-100 sample, which hinders SMX molecules access to active sites due to high flow resistances. However, as the pore diameter increases to 131.4 nm, the accessibility of SMX molecules to active sites improves, augmenting adsorption capacity and reducing the  $H_{\text{MTZ}}$  values, thereby enhancing adsorption performance. Nevertheless, further increasing the pore diameter from 131.4 to 157.1 nm resulted in a wide enough pore diameter to enable SMX molecules access, similar to 131.4 nm. However, this enlargement leads to a reduction in adsorption surface area, evidenced by the decrease in  $S_{\text{ext}}(\text{Hg})$  value. Consequently, there is an increase in  $H_{\text{MTZ}}$  from 0.73 to 1.48 cm, indicating a compromise in adsorption performance due to the reduction in surface area despite widened pore access.

The effect of channel geometry of the 3D-printed carbon monolith adsorbents, comparing conventional straight and interconnected network channels, on the dynamic adsorption performance of SMX is illustrated in Figure 10.12. In this study, the R/Cs

ratio was maintained at 1000. Breakthrough curve data were collected at specific volumetric flow rates to ensure similar residence times in both monolith configurations.



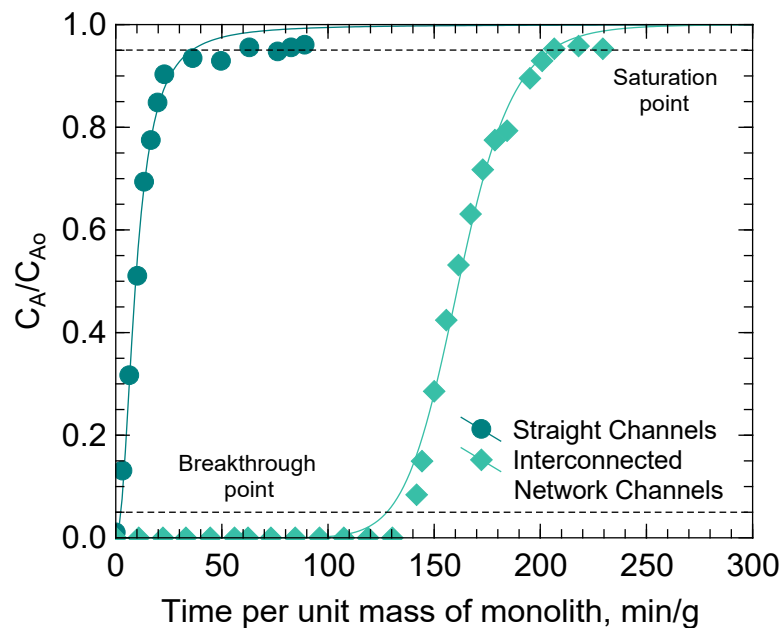
**Figure 10.11.** Variation of the uptake of SMX adsorbed at the breakthrough point and  $H_{MTZ}$  with the pore diameter.

For the straight channel monolith (Exp. No. 9), a flow rate of 0.58 mL/min was used, while the interconnected network channel monolith (Exp. No. 5) operated at 0.29 mL/min. Both configurations achieved residence times close to 50 seconds. Figure 10.12 reveals significant differences in breakthrough behavior between the two designs, highlighting the importance of channel configuration alongside porous texture accessibility in influencing dynamic adsorption performance.

The straight channel monolith exhibited a rapid breakthrough at approximately 5 min, whereas the interconnected network channel monolith delayed breakthrough until 200 min. The  $H_{MTZ}$  for the straight channeled monolith was 2.2 cm, nearly matching the monolith's total length of 2.3 cm. In contrast, the  $H_{MTZ}$  for the interconnected network channeled monolith was substantially shorter at 0.73 cm.

The early breakthrough observed in the straight channel configuration is attributed to preferential pathways, where SMX flows linearly, promoting laminar flow.

This geometry reduces interaction between the liquid phase and the monolithic adsorbent, thereby limiting diffusion within the designed porous macrostructure and resulting in poor adsorption performance. On the other hand, the interconnected network channel design induces a more complex flow pattern, generating turbulence that enhances diffusion throughout the porous macrostructure. This advanced geometry significantly improves adsorption performance, as evidenced by the much longer breakthrough time compared to straight channel geometry. A similar behavior was reported by Chaparro-Garnica et al. (2021b), who manufactured CuO/CeO<sub>2</sub> 3D-printed carbon monolithic supports with conventional honeycomb channels and advanced tortuous channels for the preferential oxidation of CO in the presence of H<sub>2</sub>. They found that the tortuous design favored active phase-gas contact and improved gas diffusion within the pores.



**Figure 10.12.** Effect of channel geometry on breakthrough curves for SMX adsorption on 3D-printed carbon monoliths. The lines represent the BDST model.

## 10.4 Conclusions

Novel 3D-printed carbon monolith adsorbents with diverse channel geometries and porous textures were successfully designed and fabricated using an innovative

hybrid method that integrates sol-gel polymerization with 3D printing technology. These monoliths were specifically engineered for the dynamic adsorption of SMX from water. Both interconnected network channels and conventional straight channels were effectively realized, each offering distinct advantages for fluid flow and mass transfer.

The monolithic structures exhibited optimal integration and structural integrity, with precisely controlled channel geometries within the carbon bulk, achieved through advanced 3D printing technology. The synthesis conditions, particularly the R/Cs ratio, played a crucial role in determining the morphological, textural and mechanical properties, directly influencing their adsorption performance.

Increasing the R/Cs ratio resulted in larger spherical primary particles, which modulated pore diameter and skeleton size within the macropore region (ranging from 95.1 to 157.1 nm). This adjustment enhanced accessible macroporosity and reduced flow resistance, thereby improving the monolith's performance as adsorbents. Batch adsorption isotherms demonstrated a maximum adsorption capacity of 61.4 mg/g for Monolith-100, attributed to  $\pi$ - $\pi$  stacking and electrostatic attractions. In dynamic adsorption, a different trend was observed: Monolith-1000 > Monolith-500 > Monolith-100 > Monolith-2000. Increasing the R/Cs ratio improved SMX accessibility, leading to enhanced breakthrough times and reduced  $H_{MTZ}$  values, despite the reduction in  $S_{ext}(Hg)$ . However, an excessively high R/Cs ratio (Monolith-2000) compromised overall adsorption performance by significantly reducing breakthrough times.

The channel geometry of the monoliths significantly influenced breakthrough times. The complex network of interconnected channels exhibited enhanced turbulence and mixing, promoting better mass transfer and diffusion of SMX throughout the porous structure. In contrast, the conventional straight channels showed a more laminar flow pattern, leading to preferential pathways and limited interaction with the adsorbent material.

The findings demonstrate the potential utility of sol-gel polymerization and 3D printing technology to engineer advanced adsorbent structures with customizable properties, enabling a transition from conventional packed beds to 3D printed monolithic beds, marking a significant evolution in adsorption technology.

# CHAPTER

# 11

**3D-PRINTED MONOLITHIC  
ACTIVATED CARBONS FOR THE  
ADSORPTION OF  
SULFAMETHOXAZOLE FROM  
WATER: INFLUENCE OF  
ACTIVATION TIME AND CHANNEL  
GEOMETRY ON ADSORPTION  
CAPACITY AND BREAKTHROUGH  
CURVES**

## **11.1 Introduction**

Monoliths are increasingly recognized as highly promising nanostructured porous materials for industrial applications due to their unique architecture (Hossain et al., 2022; Nguyen et al., 2020; Parsa et al., 2023; Querejeta et al., 2022). These structures consist of thin, vertical, parallel channels of various shapes, including circular, square, triangular and hexagonal (Avila et al., 2005). These channels are separated by walls and interconnected through a sophisticated network of macropores, collectively reducing flow resistance (Tomašić and Jović, 2006).

In comparison to traditional packed bed columns that use pellets or powders, monoliths offer several superior attributes: enhanced mass transfer, reduced pressure drops, exceptional thermal stability and impressive mechanical strength. These properties make monoliths particularly suitable for advanced environmental remediation applications, such as adsorption (Govender and Friedrich, 2017; Hosseini et al., 2020).

Conventional monolith fabrication, often referred to as honeycomb monolith production, typically involves extruding a paste composed of the material, binders, and organic and inorganic fillers, followed by a carbonization process (Lim et al., 2010). Unfortunately, this method restricts channel geometry to straight configurations and often results in significant shrinkage and inconsistent porosity, leading to structural imperfections. The lack of uniform porosity and precise control over channel geometry limits fluid dynamics to laminar flow within the channels (Vergunst et al., 2001). This limitation inhibits effective fluid mixing and distribution, causing preferential flow paths and channeling issues, which reduces adsorbate-adsorbent interaction, thereby limiting their efficiency as monolithic adsorbents (Kovacev et al., 2021).

Achieving meticulous control over porosity and channel geometry during monolith fabrication is therefore crucial. Ensuring uniform porosity and precise channel geometry is essential for optimizing fluid dynamics, enhancing mass transfer, and mitigating issues such as preferential flow and channeling. Innovations in fabrication methodologies are critical for producing monoliths with highly controlled and integral structures, thereby maximizing their efficiency. Recently, a pioneering hybrid

methodology that combines sol-gel polymerization with 3D printing technology has emerged as an innovative technique for developing monoliths with meticulously controlled porosity and channel geometry.

Sol-gel polymerization facilitates the creation of integral carbon gels, nanostructured carbon materials of high purity, where their shape, chemical composition, particle size and pore size distribution can be precisely engineered and controlled (Pekala, 1989). Meanwhile, 3D printing enables the fabrication of three-dimensional prototypes and structures from digital files, where the solid modelling component of Computer-Aided Design (CAD) forms the basis for additive technology. This approach utilizes additive models to build layers of extremely thin cross-sectional areas, enabling the manufacture of intricate and complex shapes and surfaces that are very difficult to achieve using conventional methods (Jandyal et al., 2022). This integration not only facilitates precise control over porosity but also allows the design and creation of complex channel geometries with exact dimensions, shapes, alignments and configurations (Praveena et al., 2022).

Previous studies have demonstrated the effectiveness of these combined techniques. For instance, Chaparro-Garnica et al. (2021b) manufactured CuO/CeO<sub>2</sub> 3D-printed carbon monolithic supports with both conventional honeycomb channels and advanced tortuous channels for the preferential oxidation of CO in the presence of H<sub>2</sub>. Their findings demonstrated that the tortuous design significantly enhanced active phase-gas contact and gas diffusion within the pores, resulting in superior catalytic performance compared to conventional honeycomb supports. Similarly, Parra-Marfil et al. (2024) engineered auto-pressurized carbon Ni/CeO<sub>2</sub> microreactors with Tesla-valve-shaped channels for CO<sub>2</sub> methanation, achieving superior catalytic activity compared to traditional straight-channel monolithic microreactors.

The recent application of these advanced techniques to produce 3D-printed monoliths for gas-phase applications has introduced a novel method for creating ordered monolithic beds optimized for liquid-phase adsorption. This innovative approach transforms fixed bed systems into monolithic structures with controlled porosity and channel geometry, improving fluid distribution within the monolith,



promoting contact between the fluid and active sites, and providing precise control over fluid dynamics. These advancements contribute to higher adsorption capacities and improved mass transport properties, significantly enhancing adsorption efficiency and operational stability.

Chapter 11 focuses on the manufacture of 3D-printed activated carbon monoliths using CO<sub>2</sub> and H<sub>2</sub>O as activating agents, featuring different 3D channel geometry CAD prototypes, including straight, rhomboidal, hexagonal and interconnected network shapes. This innovative hybrid method combines sol-gel polymerization of resorcinol (R), formaldehyde (F), water (W) and Cs<sub>2</sub>CO<sub>3</sub> (Cs) as a catalyst, with advanced 3D printing technology. The performance of these fabricated monoliths was evaluated in the adsorption of sulfamethoxazole, a hazardous antibiotic frequently detected in water (Grenni et al., 2019). The effects of activating agents and activation times were analyzed in both batch and continuous operations using adsorption isotherms and breakthrough curves. The influence of channel geometry was assessed through breakthrough curves and validated by Computational Fluid Dynamics (CFD) simulations, elucidating the observed adsorption behavior.

## **11.2 Experimental methodology**

### **11.2.1 Design of 3D geometry prototypes using Computer-Aided Design (CAD)**

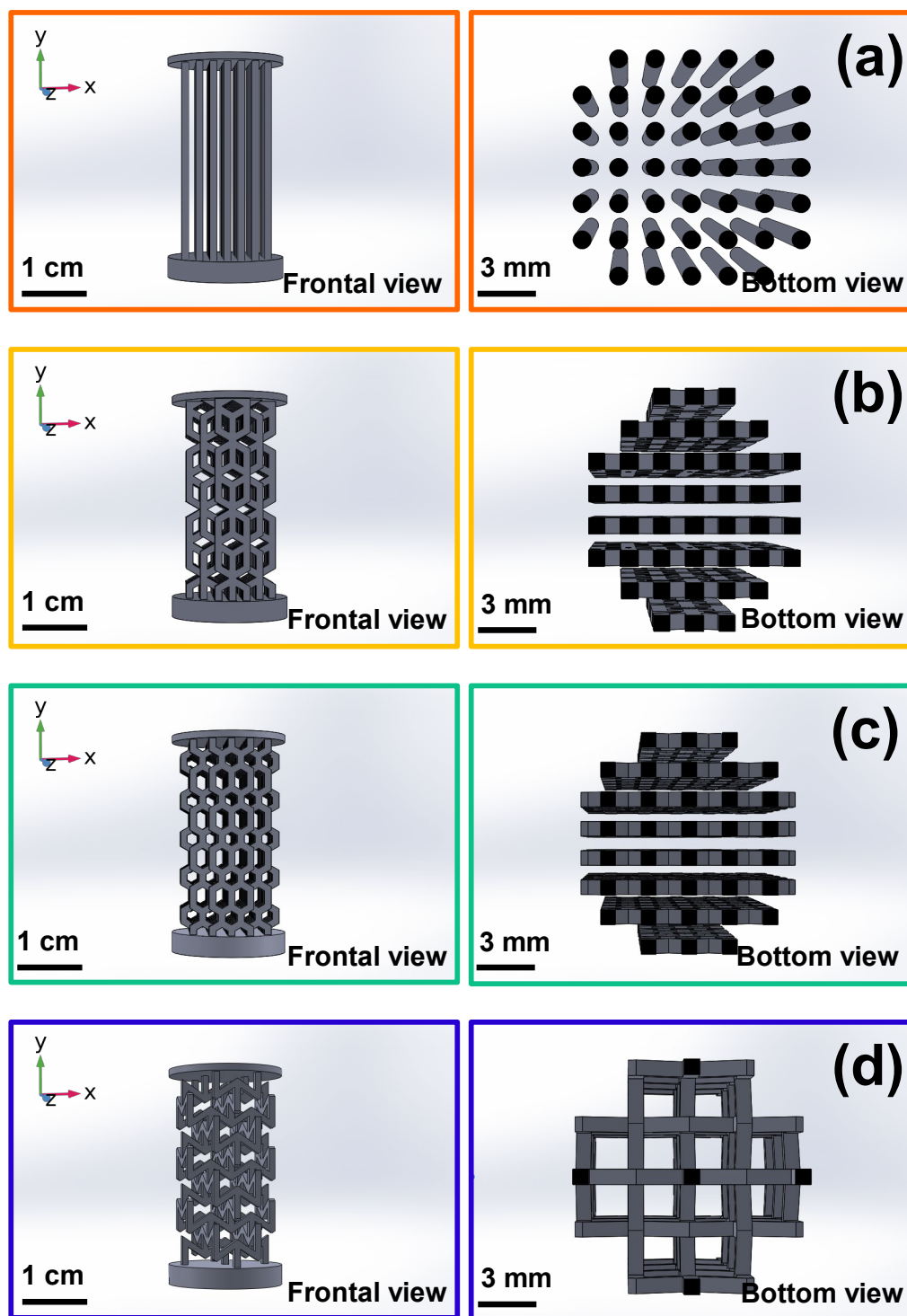
Highly detailed prototypes of 3D CAD models were meticulously developed using SolidWorks software to accurately represent the channel geometries of the monoliths, as presented in Figure 11.1, offering both frontal and bottom views. The channel geometries include a conventional straight channel as a reference geometry, and three complex advanced geometries named rhomboidal, hexagonal and interconnected network.

The straight channel geometry, depicted in Figure 11.1 (a), consists of single channels aligned vertically and separated by walls, similar to the conventional honeycomb monoliths fabricated via extrusion. Figure 11.1 (b) presents a more complex geometry, featuring a tortuous path of interconnected channels resembling diamonds and rhomboids, which form a repeating pattern along the y-direction. Figure

11.1 (c) shows another intricate geometry composed of interconnected channels resembling symmetric and elongated hexagons, combined to form a hexagonal pattern within the monolith. The main characteristic of these two complex geometries is that the tortuous paths are formed by layers that create the pattern, with these layers, separated by integrated carbon walls, repeating the pattern along the z-direction, as seen in the bottom views. Finally, Figure 11.1 (d) presents channels arranged in a complex network of interconnected paths in multiple directions, traversing vertically and horizontally, resembling an interconnected array pattern. These sophisticated prototypes of channel geometries were then materialized using an Ultimaker 3D printer, model S3, employing a co-polyester transparent filament for optimal fidelity and clarity.

### **11.2.2 Integration of sol-gel process and 3D printing technology for fabricating 3D-printed carbon monoliths**

The fabrication of 3D-printed activated carbon monoliths was achieved using an hybrid method that combines sol-gel polymerization with advanced 3D printing technology, as described in Section 10.2.2. Solutions of resorcinol (R), formaldehyde (F), water (W) and  $\text{Cs}_2\text{CO}_3$  (Cs) were then prepared in specific molar ratios:  $R/F = 1/2$ ,  $R/W = 1/15$  and  $R/Cs = 500$ . These solutions, along with the 3D-printed templates, were cast into cylindrical glass molds and hermetically sealed. The polymerization and curing process included 1 day at ambient temperature, followed by 1 day at 50 °C, and finally 5 days at 80 °C. After gelation and curing, the polymeric monoliths were demolded, cut to the desired dimensions, and immersed in a 2 M acetic acid solution for 1 day. The water within the developed porosity was then replaced with acetone over a 3-day period, with solution changes performed twice daily. This formed organic monoliths with the 3D-printed template seamlessly integrated into the organic gel matrix. The organic monoliths were air-dried at room temperature before undergoing carbonization in a  $\text{N}_2$  flow of 150 mL/min. Carbonization was conducted for 2 h at 300 °C, followed by an additional 2 h at 850 °C, with controlled heating rate of 1.5 °C/min. During this process, the 3D-printed template was eliminated, leaving behind the intricate channel geometry in the resulting carbon monoliths.



**Figure 11.1.** 3D CAD prototypes of advanced geometries representing straight channels (a), rhomboidal channels (b), hexagonal channels (c) and interconnected network channels (d), shown with frontal and bottom views.

### 11.2.3 Activation of 3D-printed carbon monoliths using CO<sub>2</sub> and H<sub>2</sub>O

The fabricated 3D-printed monoliths configured with interconnected network channel geometry were physically activated using CO<sub>2</sub> and water steam (H<sub>2</sub>O) at 850 °C. The procedures for each activation method are detailed as follows. For CO<sub>2</sub> activation, a flow rate of 60 mL/min was applied for durations of 2, 4, 6 and 8 h. This resulted in activated carbon monoliths with burn-off percentages ranging from 3.1 to 13.3 %. H<sub>2</sub>O activation was performed using a vertical quartz tube evaporator enclosed in an electrical resistance heater, which was attached at the entrance of the furnace. A N<sub>2</sub> stream of 100 mL/min was administered at the bottom of the evaporator, while 0.1 mL/min of liquid water was introduced at the top of the evaporator using a peristaltic pump. The water steam generated in the evaporator was then fed into the furnace. The monoliths were activated for durations of 0.5, 1, 1.5 and 2 h, resulting in burn-off percentages ranging from 8.5 to 26.7 %. It is important to highlight that carbon monoliths were not activated for longer times due to the loss of structural integrity during activation process. The 3D-printed activated carbon monoliths from CO<sub>2</sub> activation (series A) and H<sub>2</sub>O activation (series B) were designated as Monolith A-2h, Monolith A-4h, Monolith A-6h and Monolith A-8h for CO<sub>2</sub> activation at 2, 4, 6 and 8 h, respectively, and Monolith B-0.5h, Monolith B-1h, Monolith B-1.5h and Monolith B-2h for water steam activation at 0.5, 1, 1.5 and 2 h, respectively. A non-activated 3D-printed carbon monolith was also fabricated as a reference.

### 11.2.4 Characterization of 3D-printed monolithic activated carbons

Photomicrographs of the activated carbon monoliths was taken using scanning electron microscopy with a Quanta 400 FEI microscope, visualizing morphologies over the channel surface and bulk carbon.

N<sub>2</sub> adsorption-desorption isotherms at -196.15 °C were obtained in a TriStar II Plus Micromeritics analyzer, while Hg intrusion porosimetry curves were acquired using an AutoPore V Micromeritics Hg porosimeter. The surface area of the monoliths ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{p}}$ ) and volume of micropores ( $V_{\text{mic}}$ ) were estimated by applying Brunauer, Emmet and Teller method (Brunauer et al., 1938), Gurvich rule at  $P/P^0 =$

0.99 and Dubinin-Radushkevich equation, respectively. The Stoeckli equation was used to calculate the mean pore width ( $L_0$ ) and area of micropores ( $S_{mic}$ ) using  $N_2$  adsorption data (Rouquerol et al., 1998).  $S_{meso}$  was obtained subtracting  $S_{micro}$  from  $S_{BET}$  and  $V_{meso}$  subtracting  $V_{micro}$  from  $V_p$ . The pore size distribution (PSD) in the macropore region was determined using Hg porosimetry data.

#### **11.2.5 Sulfamethoxazole characteristics and quantification**

Sulfamethoxazole (SMX) (CAS: 723-46-6) was employed in this work as a model compound to evaluate the adsorption performance of the 3D-printed activated carbon monoliths. The detailed physicochemical properties of SMX are listed in Table 9.1. At a neutral pH of 7, SMX predominantly exists in its anionic form, characterized by  $\pi$ -acceptors located in both the functional amino group and the N-heteroaromatic ring, as illustrated in Figure 9.1. Below a pH of 5.7, SMX transitions to its cationic and neutral forms.

The use of a UV-Vis spectrophotometric method enables consistent and reproducible quantification of SMX, thereby ensuring the validity of the adsorption performance results for the 3D-printed activated carbon monoliths. The quantification was accurately using a Shimadzu UV-Vis spectrophotometer, model 2600i, set at a wavelength of 264 nm. Calibration curves were prepared across a concentration range of 1 to 20 mg/L to ensure precise measurement.

#### **11.2.6 Experimental method for obtaining adsorption isotherms**

The evaluation of the adsorption capacity of the 3D-printed monolithic activated carbons was conducted following the procedure detailed in Chapter 10, Section 10.2.5. Adsorption isotherms were obtained by plotting  $q$  vs.  $C_{Ae}$ , and the key variables in these experiments were the type of activating agent used ( $CO_2$  and  $H_2O$ ) and the activation time.

### 11.2.7 Method for obtaining breakthrough curves data

Experimental data for breakthrough curves of SMX adsorption on the 3D-printed monolithic activated carbons was collected using a monolithic packed bed adsorber, as depicted in Figure 10.2. The procedure for obtaining the experimental data adhered to the guidelines outlined in Section 10.2.6.

In these experiments, all other variables were maintained constant during the experiments to isolate the effects of the activating agent and activation time on breakthrough curves. Additionally, the effect of channel geometry on the breakthrough curves was also analyzed.

### 11.2.8 Mathematical model for fluid hydrodynamics

Fluid hydrodynamics for SMX adsorption on 3D-printed activated carbon monoliths with various advanced channel geometries were analyzed using COMSOL Multiphysics, a comprehensive finite element analysis software. The study aimed to simulate the fluid dynamics under turbulent flow conditions to understand and optimize the adsorption process within the monolithic structures.

The mathematical model employs partial differential equations to describe the momentum balance, liquid-phase mass balance, turbulent kinetic energy balance and turbulence dissipation rate balance. The  $\kappa$ - $\epsilon$  turbulence model is used to simulate the mean flow characteristics of the turbulent flow within the designed channel geometries.

The momentum balance equation is given by the Navier-Stokes equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p \mathbf{I} + (\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T)] \quad (11.1)$$

The liquid-phase mass balance is described by the continuity equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (11.2)$$

The balance for turbulent kinetic energy is:

$$\rho \frac{\partial \kappa}{\partial t} + \rho(\mathbf{u} \cdot \nabla) \kappa = \nabla \cdot \left[ \left( \mu + \frac{\mu_T}{\sigma_\kappa} \right) \nabla \kappa \right] + P_\kappa - \rho \epsilon \quad (11.3)$$

The equation for the turbulence dissipation rate is:

$$\rho \frac{\partial \varepsilon}{\partial t} + \rho(u \cdot \nabla) \varepsilon = \nabla \cdot \left[ \left( \mu + \frac{\mu_T}{\sigma_\varepsilon} \right) \nabla \varepsilon \right] + C_{\varepsilon 1} \frac{\varepsilon}{\kappa} P_\kappa - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{\kappa} \quad (11.4)$$

The turbulent viscosity is defined as:

$$\mu_T = \rho C_\mu \frac{\kappa^2}{\varepsilon} \quad (11.5)$$

The rate of deformation term is expressed as:

$$P_\kappa = \mu_T [\nabla u : (\nabla u + (\nabla u)^T)] \quad (11.6)$$

To solve the mathematical model numerically, the following initial (IC) and boundary conditions (BC) were applied:

$$\text{IC: } t = 0 \quad u = 0 \text{ m/s; } p = 0 \text{ Pa} \quad (11.7)$$

$$\text{BC: } \text{At the inlet of the monolith: } u = -\frac{Q \times 100}{A_c \times 60} \cdot n \quad (11.8)$$

$$\text{BC: } \text{At the outlet of the monolith: } p = 101,325 \text{ Pa} \quad (11.9)$$

$$\text{BC: } \text{On the walls of the monolith channels: } u = 0 \quad (11.10)$$

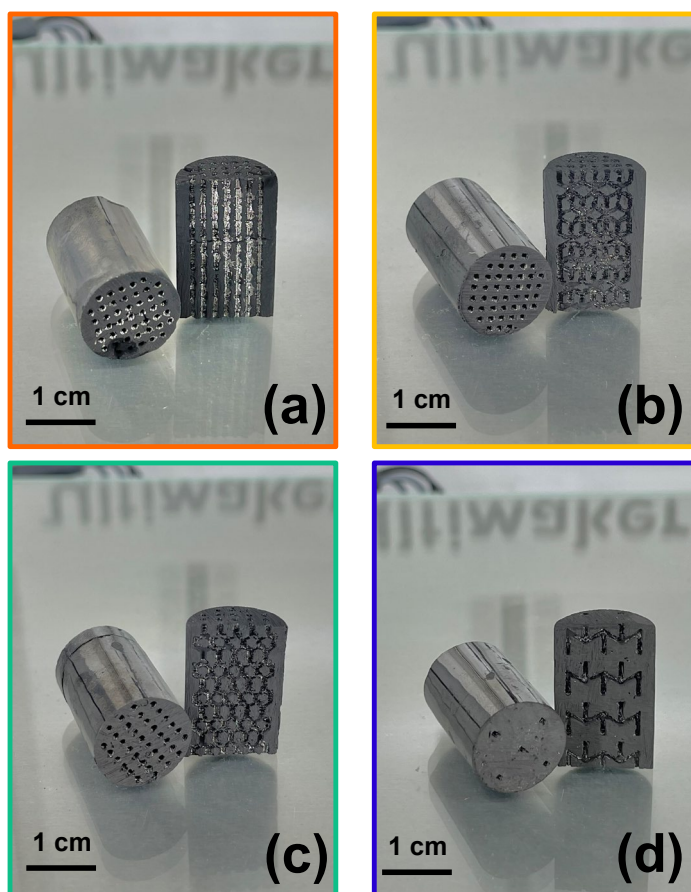
where  $u$  is the velocity vector of the SMX solution, m/s;  $\rho$  is the fluid mass density, kg/m<sup>3</sup>;  $p$  is the pressure, Pa;  $\mu$  is the dynamic viscosity, Pa s;  $\mu_T$  is the turbulent viscosity, Pa s;  $\kappa$  is the turbulent kinetic energy, m<sup>2</sup>/s<sup>2</sup>;  $\varepsilon$  is the turbulence dissipation rate, m<sup>2</sup>/s<sup>3</sup>;  $P_\kappa$  is the rate of deformation term;  $\sigma_\varepsilon$  and  $\sigma_\kappa$  are turbulent Prandtl numbers for  $\kappa$  and  $\varepsilon$ , respectively;  $C_{\varepsilon 1}$ ,  $C_{\varepsilon 2}$  and  $C_\mu$  are empirical constants for  $\kappa$ - $\varepsilon$  turbulence model,  $t$  is the time, s;  $Q$  is the volumetric flow rate, mL/min;  $A_c$  is the cross-sectional area of the channels, cm<sup>2</sup>.

## 11.3 Results and discussion

### 11.3.1 Characterization of the 3D-printed monolithic activated carbons

Figure 11.2 depicts the fabricated 3D-printed carbon monoliths with different channel geometries, activated with H<sub>2</sub>O for 2 h. Monoliths activated with both H<sub>2</sub>O and CO<sub>2</sub> at different times are excluded from this figure, as no significant structural changes were observed regardless of the activating agent used and the activation time. In the figure, the 2-hour water steam activated carbon monoliths are shown alongside a transverse sectional view, revealing their channel geometries. The image

demonstrates impeccable replication of the original CAD 3D templates for all geometries (Figure 11.1). After carbonization, the 3D-printed polymer templates were entirely removed from the carbon bulk, resulting in the precise formation of intricate channel geometries within the monolithic structures. These geometries, designed and controlled through the hybrid sol-gel process combined with 3D printing technology, exhibit excellent integration and fidelity to the original 3D CAD prototypes. These results highlight the exceptional capability of 3D printing technology to accurately control and replicate complex channel geometries within monolithic structures, enabling the design and fabrication of a wide variety of previously unachievable channel structures with high precision.



**Figure 11.2.** Image representing 3D-printed carbon monoliths activated with  $\text{H}_2\text{O}$  for 2 hours, with transverse sectional view revealing straight channel (a), rhomboidal channel (b), hexagonal channel (c) and interconnected network channel geometries.



In the straight channel configuration (Figure 11.2 (a)), the channels presented a conventional linear pattern providing a direct channelized straightforward path for fluid flow, avoiding mixing and distribution of the fluid. In the rhomboidal configuration (Figure 11.2 (b)), the fluid flow follows a tortuous path that can improve distribution of the fluid, increasing mass transfer and reducing channeling effects. The same effect can be achieved with the hexagonal geometry (Figure 11.2 (c)), where the fluid intertwines along the length of the monolith, providing better distribution of the fluid. In the interconnected network channel monolith (Figure 11.2 (d)), the intricate network facilitates multiple pathways for fluid flow distribution within the monolith, thereby enhancing mass transfer and improving performance. This technological advancement highlights the potential of 3D printing technology in creating customized and high-performance monolithic structures for a multitude of applications.

SEM images of carbon monoliths displaying various structural features are depicted in Figure 11.3. Figure 11.3 (a) clearly captures the CAD-designed channel morphology, confirming the successful replication of the geometric pattern within the monolith with channel widths of 700  $\mu\text{m}$  (0.7 nm). Surface irregularities at the interface between the channel wall and the carbon bulk are evident in Figure 11.3 (b), originating from the layer-by-layer printing method that accurately reproduces the template across the monolith surface. The figures also enable the identification of three distinct regions: the morphology over the channel surface (highlighted in green), the morphology over the carbon bulk (highlighted in light blue) and the interface between the channel wall and the carbon bulk (highlighted in dark blue).

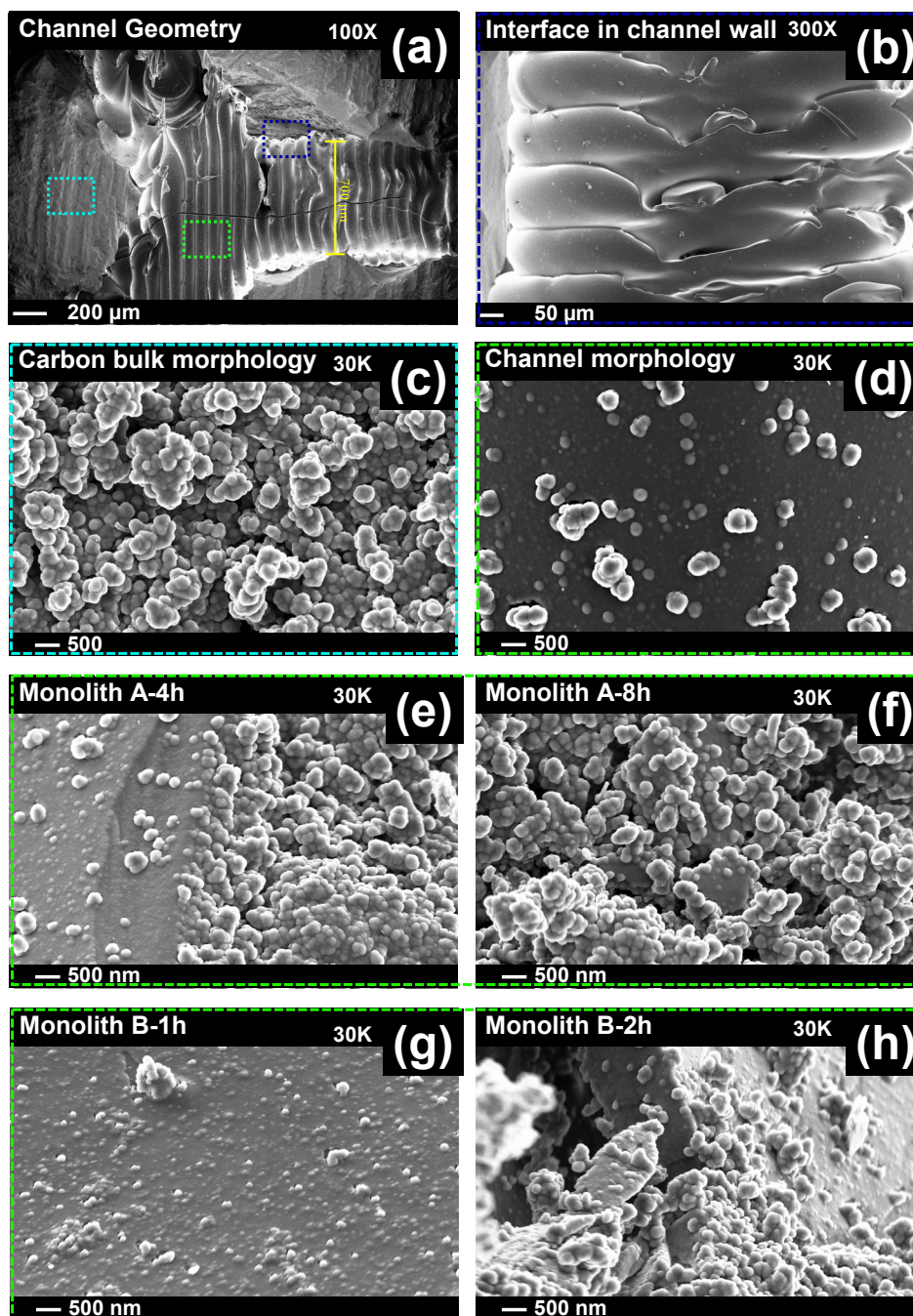
In Figure 11.3 (c), the carbon bulk morphology reveals interconnected spherical primary particles forming a three-dimensional network or skeleton within the monoliths. Chapter 9 and 10 concluded that the size of these particles can be controlled by catalyzing sol-gel polymerization with  $\text{Cs}_2\text{CO}_3$  and adjusting the R/Cs ratio to achieve monoliths with highly accessible porosity. Increasing the R/Cs ratio reduces nucleation centers, resulting in larger particle sizes. No significant differences in particle size were observed with varying activating agents and times.

Moving to Figure 11.3 (d), which depicts the morphology over the channel surface highlighted in green in Figure 11.3 (a) for the non-activated monolith, notable differences in carbon morphology compared to Figure 11.3 (c) are observed. Herein, the absence of spherical primary particles over the channel surface is evident, with only sporadic and disconnected particles present. These disparities may stem from carbon deposition left by the 3D-printed polymer template during the carbonization step. As discussed in Chapter 10, this carbon residue is known to block macropores and alter textural properties, now also affecting the surface morphology of the channel.

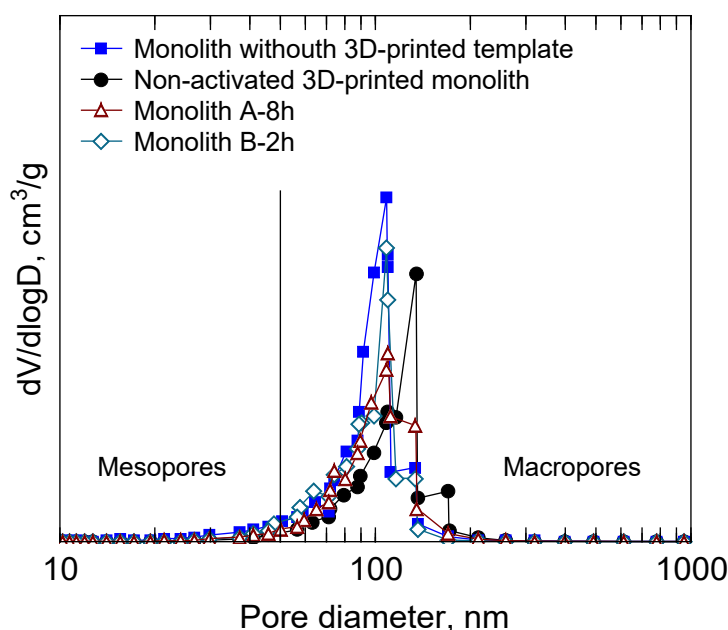
Figures 11.3 (e) and 11.3 (f) illustrate the morphology of the channel surface at different CO<sub>2</sub> activation times: 4 and 8 h, respectively. It is observed that increasing activation time substantially removes the carbon deposit from the polymer template on the channel surface. Figure 11.3 (e) shows partial removal of carbon deposit, while Figure 11.3 (f) achieves complete elimination of the polymer residue, revealing spherical primary particles over the surface of the channel, similar to those observed in Figure 11.3 (c) for the region over the carbon bulk of the monolith.

For H<sub>2</sub>O activation over 1 h, Figure 11.3 (g) shows lumps resembling spherical particles, indicating partial reduction of the carbon deposit. Increasing the activation time to 2 h, Figure 11.3 (h) displays spherical primary particles, similar to CO<sub>2</sub> activation effects, demonstrating that H<sub>2</sub>O activation also effectively eliminates the carbon deposit on the channel surface. These results indicate that while activation does not affect carbon morphology and skeleton size, it effectively removes the polymer residue left during carbonization. This removal has the potential to resolve the porosity blockage issues observed in Chapter 10 with non-activated 3D-printed carbon monoliths.

Figure 11.4 displays pore size distribution curves (PSD) derived from Hg porosimetry data for the non-activated monolith synthesized without a 3D-printed template, a non-activated 3D-printed monolith, Monolith A-8h and Monolith B-2h samples. Data of these curves at different activation times are not shown due to the absence of observable differences in pore size distribution. Furthermore, the calculated textural properties are listed in Table 11.1.



**Figure 11.3.** SEM images of carbon monoliths displaying various structural features: channel geometry (a), interface between channel wall and carbon bulk (b), carbon bulk morphology (c), channel morphology without activation (d), channel morphologies of monoliths activated with CO<sub>2</sub> for 2 and 4 h (e, f) and channel morphologies of monoliths activated with H<sub>2</sub>O for 1 and 2 h (g, h).



**Figure 11.4.** PSD curves obtained by Hg porosimetry for carbon monoliths.

The figure reveals a predominance of macropores in the carbon monoliths, which aligns with the interparticle sizes derived from spherical particles observed in SEM images. This ensures the production of monoliths with controlled skeleton and pore sizes, featuring highly accessible macroporosity and reduced flow resistances.

**Table 11.1.** Textural properties of the 3D-printed monolithic activated carbons analyzed by Hg intrusion porosimetry.

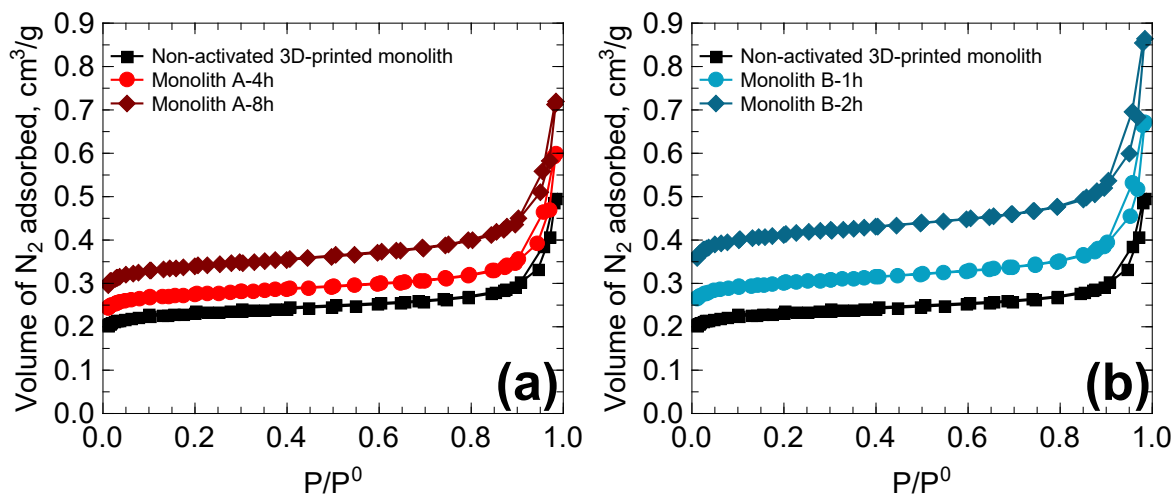
| Monoliths                            | Hg porosimetry           |                                                      |                                                     |                                                       |                                                      |                                                    |
|--------------------------------------|--------------------------|------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------|------------------------------------------------------|----------------------------------------------------|
|                                      | $D_p(\text{Hg})$<br>(nm) | $V_{\text{meso}}(\text{Hg})$<br>(cm <sup>3</sup> /g) | $S_{\text{meso}}(\text{Hg})$<br>(m <sup>2</sup> /g) | $V_{\text{macro}}(\text{Hg})$<br>(cm <sup>3</sup> /g) | $S_{\text{macro}}(\text{Hg})$<br>(m <sup>2</sup> /g) | $S_{\text{ext}}(\text{Hg})$<br>(m <sup>2</sup> /g) |
| Monolith without 3D-printed template | 84.4                     | 0.091                                                | 11.5                                                | 1.245                                                 | 51.7                                                 | 63.3                                               |
| Non-activated monolith               | 102.5                    | 0.035                                                | 3.8                                                 | 0.885                                                 | 32.1                                                 | 35.9                                               |
| Monolith A-8h                        | 87.7                     | 0.037                                                | 3.7                                                 | 0.961                                                 | 41.9                                                 | 45.7                                               |
| Monolith B-2h                        | 97.0                     | 0.063                                                | 6.8                                                 | 1.055                                                 | 40.6                                                 | 47.5                                               |

Comparing the non-activated 3D-printed monolith with the non-activated monolith synthesized without using a 3D-printed template, alterations in the textural properties are evident, particularly in the reduction of the  $S_{\text{ext}}(\text{Hg})$  value from 63.3 to 35.9  $\text{m}^2/\text{g}$ . This reduction is attributed to the blockage of porosity caused by the use of a 3D-printed template during fabrication, as discussed in Chapter 10, and also observed in SEM images (Figure 11.3 (d)). This porosity blockage represents a limitation in applying these new 3D-printed monoliths.

The PSD curves of the activated monoliths with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  show no differences in pore size distribution, indicating that activation does not affect macroporosity or the skeleton size. These results are consistent with the minimal influence on the size of spherical primary particles observed in SEM images with varying activating agents and times. Additionally, textural properties such as  $S_{\text{ext}}(\text{Hg})$ ,  $V_{\text{macro}}(\text{Hg})$  and  $V_{\text{meso}}(\text{Hg})$  increased in the activated monoliths compared to the non-activated monolith, indicating a recovery of the original macroporosity developed during fabrication. This recovery is also consistent with the removal of the carbon deposits on the channel surface of the monolith observed in SEM images, further confirming that the issues related to macroporosity blockage are resolved.

$\text{N}_2$  adsorption-desorption isotherms at  $-196.15^\circ\text{C}$  for the 3D-printed carbon monoliths are presented in Figure 11.5. The figure includes data for the non-activated 3D-printed monolith, Monolith A-4h, Monolith A-8h, Monolith B-1h and Monolith B-2h. The isotherms exhibit a combination of type Ia and IIb characteristics according to IUPAC nomenclature, indicating hierarchical porosity in the carbon monoliths, which remains unchanged regardless of the activating agent used or activation time (Rouquerol et al., 1998; Thommes et al., 2015). As discussed in Chapter 10, type Ia isotherms reveal micropores within the spherical particles observed in SEM images, while type IIb isotherms, characterized by the absence of a plateau at high  $P/P^\circ$  values, are associated with interparticle voids leading to macropores between the spherical primary particles. The narrow hysteresis loops observed in all monoliths indicate that porosity is predominantly in the macropore region, as corroborated by the PSD curves obtained through Hg porosimetry.

Significant differences in the volume of N<sub>2</sub> adsorbed were observed as the activation time increased for both CO<sub>2</sub> and H<sub>2</sub>O activations, with adsorption volume gradually increasing as activation progressed. These results suggest the development of new micropores on the surface of the monoliths and their enlargement into wider pores in both activation procedures (Korus et al., 2022). The estimated textural properties and burn-off percentages are listed in Table 11.2.

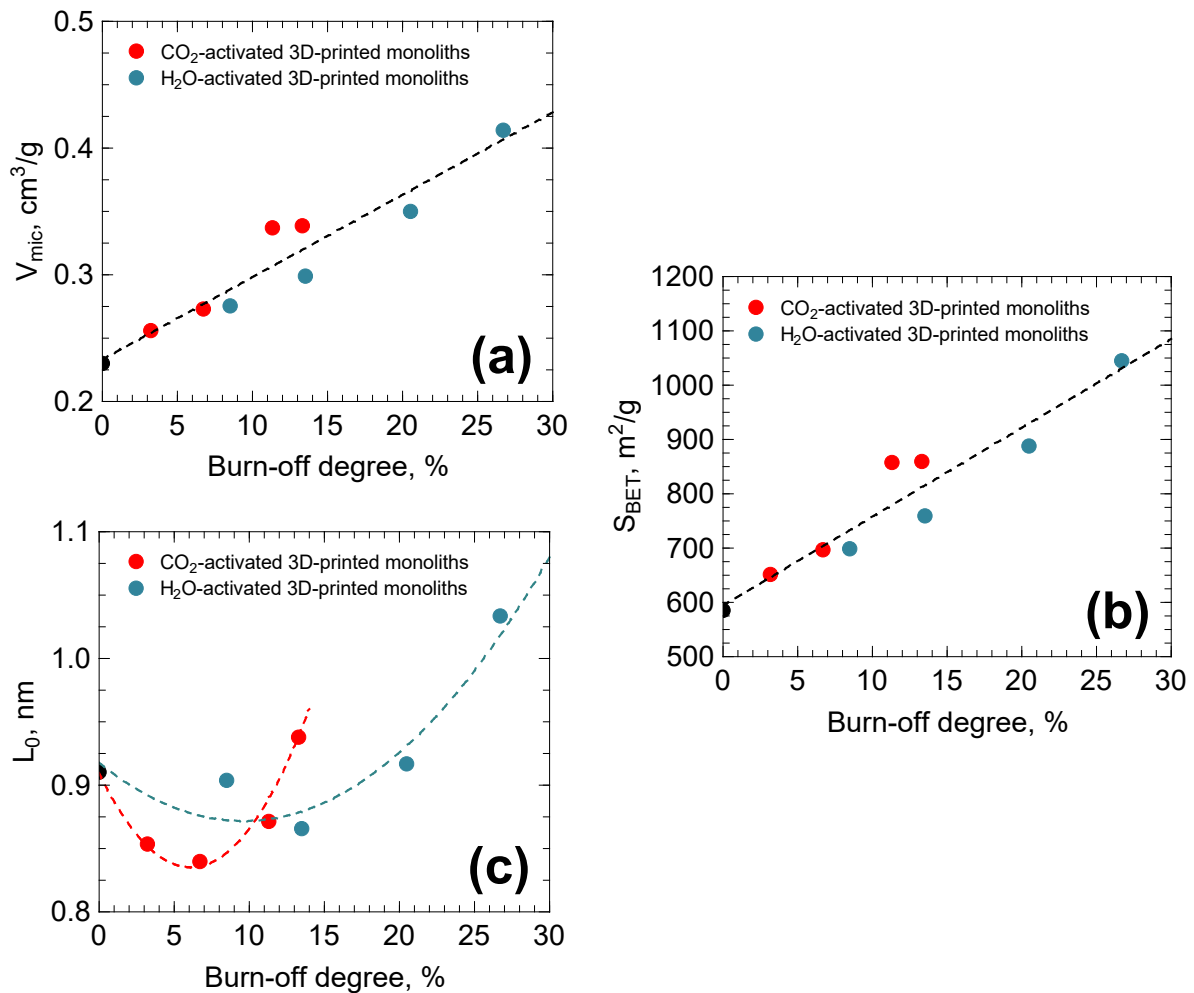


**Figure 11.5.** N<sub>2</sub> adsorption-desorption isotherms at -196.15 °C on 3D-printed carbon monoliths activated with CO<sub>2</sub> (a) and H<sub>2</sub>O (b) at different times.

**Table 11.2.** Textural properties of the 3D-printed monolithic activated carbons obtained by N<sub>2</sub> adsorption data.

| Monoliths              | N <sub>2</sub> isotherm |                                      |                                     |                     |                                      |                                       |                                       |                                        |
|------------------------|-------------------------|--------------------------------------|-------------------------------------|---------------------|--------------------------------------|---------------------------------------|---------------------------------------|----------------------------------------|
|                        | Burn-off (%)            | S <sub>BET</sub> (m <sup>2</sup> /g) | V <sub>p</sub> (cm <sup>3</sup> /g) | L <sub>0</sub> (nm) | S <sub>mic</sub> (m <sup>2</sup> /g) | V <sub>mic</sub> (cm <sup>3</sup> /g) | S <sub>meso</sub> (m <sup>2</sup> /g) | V <sub>meso</sub> (cm <sup>3</sup> /g) |
| Non-activated monolith | 0                       | 585                                  | 0.496                               | 0.91                | 508                                  | 0.230                                 | 77                                    | 0.265                                  |
| Monolith A-2h          | 3.2                     | 651                                  | 0.565                               | 0.85                | 600                                  | 0.256                                 | 51                                    | 0.309                                  |
| Monolith A-4h          | 6.7                     | 696                                  | 0.600                               | 0.84                | 651                                  | 0.273                                 | 45                                    | 0.326                                  |
| Monolith A-6h          | 11.3                    | 858                                  | 0.773                               | 0.87                | 774                                  | 0.337                                 | 84                                    | 0.435                                  |
| Monolith A-8h          | 13.3                    | 859                                  | 0.720                               | 0.94                | 723                                  | 0.339                                 | 136                                   | 0.381                                  |
| Monolith B-0.5h        | 8.5                     | 700                                  | 0.759                               | 0.90                | 610                                  | 0.276                                 | 90                                    | 0.483                                  |
| Monolith B-1h          | 13.5                    | 760                                  | 0.672                               | 0.87                | 690                                  | 0.299                                 | 70                                    | 0.373                                  |
| Monolith B-1.5h        | 20.5                    | 889                                  | 0.758                               | 0.92                | 764                                  | 0.350                                 | 125                                   | 0.408                                  |
| Monolith B-2h          | 26.7                    | 1045                                 | 0.863                               | 1.03                | 801                                  | 0.414                                 | 244                                   | 0.449                                  |

As expected, activation results in micropore widening, which is primarily responsible for the increase in  $S_{BET}$  values. For example, for the 2-hour water steam activated monolith,  $S_{BET}$  increased from 585 to 1045  $m^2/g$ . Figure 11.6 illustrates the effect of burn-off degree on  $V_{mic}$ ,  $S_{BET}$  and  $L_0$ . Figure 11.6 (a) and 11.6 (b) reveal that  $V_{mic}$  and  $S_{BET}$  increased linearly as the burn-off degree rose for both activating agents, indicating substantial opening of the micropore texture over time. It is important to note that higher burn-off degrees were obtained with  $H_2O$  activation compared to  $CO_2$  activation, highlighting that  $H_2O$  is a stronger oxidant, achieving a greater enhancement in textural properties than  $CO_2$  (Rodríguez-Reinoso et al., 1995).



**Figure 11.6.** Variation of  $V_{mic}$  (a),  $S_{BET}$  (b) and  $L_0$  (c) with the burn-off percentage for  $CO_2$  and  $H_2O$  activations.

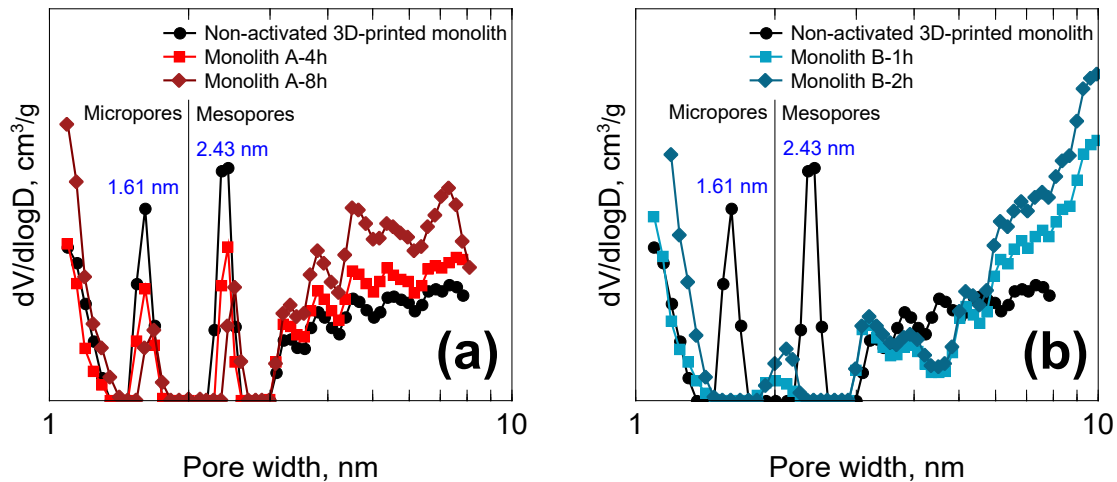
Transitioning to Figure 11.6 (c), the variation of  $L_0$  with burn-off degree reveals an interesting effect on the porous texture development of the monoliths. In  $\text{CO}_2$  activation, a decrease in  $L_0$  values is observed for Monolith A-2h and Monolith A-4h, indicating that  $\text{CO}_2$  primarily generates new microporosity at these activation times. However, further activation results in an enlargement of the microporosity width, as indicated by an increase in  $L_0$  values for activation times beyond 4 h. For  $\text{H}_2\text{O}$  activation, a similar behavior is observed, with  $L_0$  decreasing as activation time reaches 1 h and increasing after 1 h of activation. These results demonstrate that activation process on the 3D-printed carbon monoliths not only removes the carbon deposit on the channel surface, unblocking macroporosity, but also develops new, wider microporosity, dramatically increasing  $S_{\text{BET}}$ . Similar results were reported by Vivo-Vilches et al. (2015) during their study on the  $\text{CO}_2$  activation of carbon xerogels aimed at enhancing the separation of 2,2',4-trimethylpentane and n-octane.

The results mentioned above correlate well with the evolution of the PSD curves with increasing burn-off degrees, as presented in Figure 11.7 for a pore width range from 1 to 10 nm. PSD curves for  $\text{CO}_2$ -activated 3D-printed carbon monoliths, displayed in Figure 11.7 (a), reveal that activation starts from the micropore region, particularly the peak at 1.61 nm, and extends to the mesopore region, identified by the peak at 2.43 nm and pore widths above 3 nm. The gradual enlargement of these pores is indicated by the displacement of the peaks at 1.61 and 2.43 nm to larger sizes, accompanied by a decrease in the height of these pore peaks as activation time increases. Furthermore, mesopores above 3 nm, initially present in the monolith, exhibit a significant increase in their pore distribution while maintaining their pore widths.

$\text{H}_2\text{O}$  activation developed larger pores in the 3D-printed carbon monoliths compared to  $\text{CO}_2$  activation. The peaks at 1.61 and 2.43 nm, illustrated in Figure 11.7 (b), show a more pronounced displacement to larger pore sizes, shifting the entire pore distribution into the narrow mesopore region. The pore size distribution for pore widths above 3 nm also tends to shift to larger widths, with the height of the peaks in this region increasing considerably with activation time. These results are consistent with the



increasing  $S_{\text{BET}}$  and  $S_{\text{meso}}$  values observed in Table 11.2, which rise with  $\text{H}_2\text{O}$  activation.



**Figure 11.7.** PSD curves obtained by QSDFT calculations of the  $\text{N}_2$  adsorption data for carbon monoliths activated with  $\text{CO}_2$  (a) and  $\text{H}_2\text{O}$  (b) at different times.

### 11.3.2 Adsorption isotherms of SMX on the 3D-printed monolithic activated carbons

The adsorption capacity of the 3D-printed monolithic activated carbons for SMX in aqueous solutions was evaluated through adsorption equilibrium isotherms, which are essential for understanding the dynamic behavior of the monoliths. Experiments were conducted using representative pieces of the monoliths, with variations in activating agent, both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and activation times.

Experimental data for adsorption equilibrium were interpreted using three isotherm models: Freundlich, Langmuir and Radke-Prausnitz. The corresponding models involved Equations (4.9-4.11) as outlined in Chapter 4. The calculated isotherm parameters and their corresponding average percentage deviations ( $\%D_{\text{ai}}$ ) for SMX adsorption on the monolithic adsorbents are listed in Table 11.3.

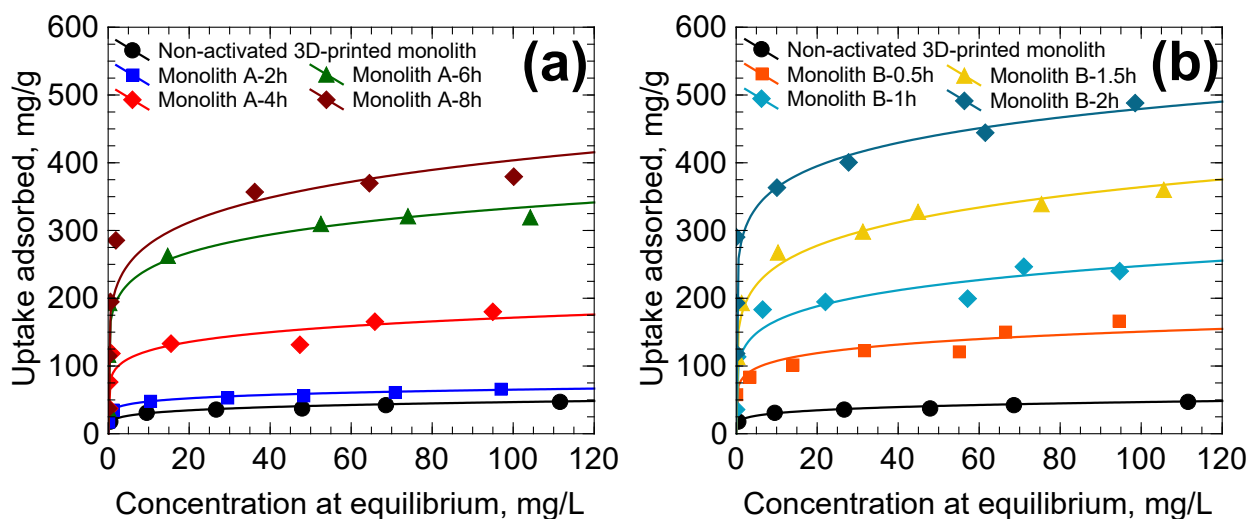
From these data, it is evident that the Langmuir model did not satisfactorily interpret the experimental data, as it registered average deviation percentages above 10 % in most cases. Although the Radke-Prausnitz model showed lower average deviation percentages, the Freundlich model provided the best interpretation of the

experimental data, exhibiting the lowest average deviation percentages in 6 out of 9 cases. Consequently, the Freundlich model was used to interpret the adsorption experimental data for all adsorbents.

**Table 11.3.** Parameters and average percentage deviation of adsorption isotherms of SMX on 3D-printed monolithic activated carbons at pH = 7, I = 0.01 N and T = 25 °C.

| Monoliths              | Langmuir        |             |                  | Freundlich                                         |       |                  | Radke-Prausnitz |                                         |      |                  |
|------------------------|-----------------|-------------|------------------|----------------------------------------------------|-------|------------------|-----------------|-----------------------------------------|------|------------------|
|                        | $q_m$<br>(mg/g) | K<br>(L/mg) | %D <sub>ai</sub> | $k_F$<br>(mg <sup>1-1/n</sup> L <sup>1/n</sup> /g) | $n_F$ | %D <sub>ai</sub> | a<br>(L/g)      | b<br>(L <sup>β</sup> /mg <sup>β</sup> ) | β    | %D <sub>ai</sub> |
| Non-activated monolith | 42.48           | 1.252       | 14.3             | 19.74                                              | 5.3   | 4.4              | 413.3           | 19.999                                  | 0.81 | 4.9              |
| Monolith A-2h          | 59.63           | 1.179       | 20.4             | 34.84                                              | 7.4   | 2.0              | 1999            | 55.609                                  | 0.87 | 9.1              |
| Monolith A-4h          | 154.61          | 2.761       | 14.7             | 87.46                                              | 6.8   | 10.5             | 847.3           | 7.631                                   | 0.91 | 12.3             |
| Monolith A-6h          | 297.47          | 13.530      | 18.2             | 177.82                                             | 7.3   | 7.5              | 9274            | 41.430                                  | 0.92 | 7.7              |
| Monolith A-8h          | 364.65          | 2.662       | 14.2             | 193.35                                             | 6.3   | 8.6              | 2469            | 9.432                                   | 0.91 | 8.6              |
| Monolith B-0.5h        | 125.13          | 52.589      | 17.0             | 76.59                                              | 6.8   | 11.5             | 56384           | 733.27                                  | 0.85 | 11.9             |
| Monolith B-1h          | 217.81          | 2.468       | 8.2              | 112.65                                             | 5.8   | 8.7              | 35036           | 307.64                                  | 0.83 | 22.3             |
| Monolith B-1.5h        | 330.01          | 1.019       | 7.5              | 167.55                                             | 5.9   | 6.9              | 744.7           | 3.443                                   | 0.89 | 1.9              |
| Monolith B-2h          | 426.45          | 13.267      | 12.6             | 275.13                                             | 8.3   | 13.8             | 7969            | 25.610                                  | 0.91 | 7.3              |

The effect of the activating agent and activation time on the adsorption isotherms of SMX on the 3D-printed monolithic activated carbons is depicted in Figure 11.8. Experiments were conducted at pH = 7 and T = 25 °C. The figure illustrates that the adsorption capacity of the monoliths for SMX increased significantly with increasing activation time for both CO<sub>2</sub> and H<sub>2</sub>O. In Figure 11.8 (a), the CO<sub>2</sub>-activated 3D-printed monoliths showed a gradual increase in SMX uptake with activation time. The maximum adsorption capacity reached 379.1 mg/g in the Monolith A-8h sample, marking an impressive 7.2-fold enhancement compared to the non-activated monolith. For steam-activated 3D-printed monoliths, Figure 11.8 (b) exhibited a similar increasing trend in adsorption capacity with activation time, showing an even more pronounced effect than CO<sub>2</sub> activation. The maximum adsorption capacity was 488.6 mg/g in the Monolith B-2h sample, representing a remarkable 9.2-fold increase over the non-activated monolith and a 1.3-fold increase compared to Monolith A-8h.



**Figure 11.8.** Adsorption isotherms of SMX on 3D-printed monolithic activated carbons from CO<sub>2</sub> (a) and H<sub>2</sub>O (b) at pH = 7 and T = 25 °C. The lines represent the Freundlich isotherm.

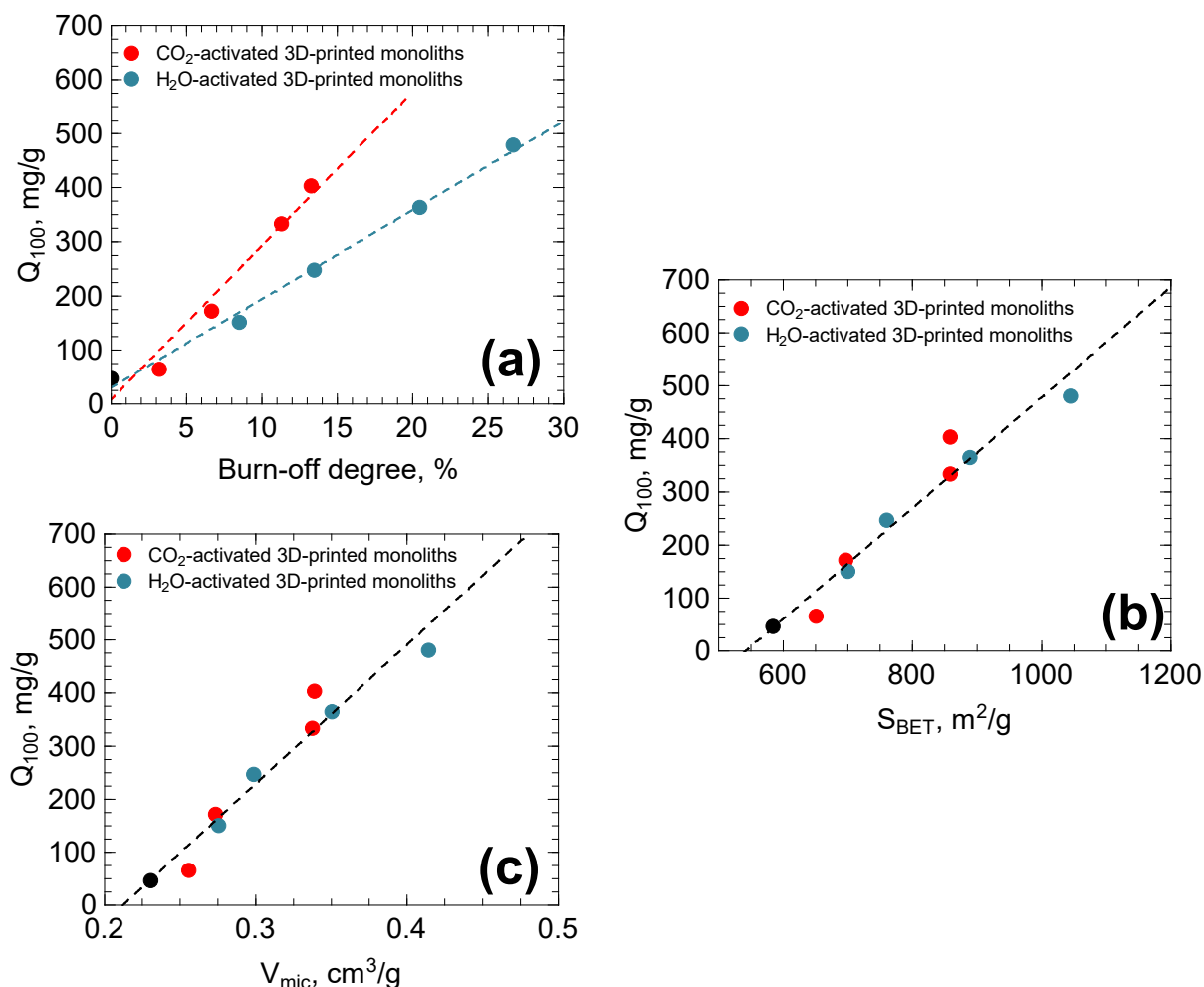
The adsorption capacities of these newly developed 3D-printed monoliths for SMX significantly exceed those reported in the literature for various other adsorbent materials (Table 11.4), including the capacity obtained by Moral-Rodríguez et al. (2016) for granular activated carbon F400.

Figure 11.9 illustrates the impact of burn-off degree on adsorption capacity at an equilibrium concentration of 100 mg/L,  $Q_{100}$ , as well as  $S_{BET}$  and  $V_{mic}$  on  $Q_{100}$ . Figure 11.9 (a) shows a linear increase in adsorption capacity with increasing burn-off percentages for both CO<sub>2</sub> and H<sub>2</sub>O activations. Notably, H<sub>2</sub>O activation requires higher burn-offs to achieve high adsorption capacities compared to CO<sub>2</sub> activation, which achieves increased adsorption capacity with lower burn-offs. Figures 11.9 (b) and 11.9 (c) demonstrate that adsorption capacity ( $Q_{100}$ ) increases with increments in  $S_{BET}$  and  $V_{mic}$ , respectively. The figures show that adsorption capacity rises linearly as these textural properties increase. This linear relationship is attributed to  $\pi$ - $\pi$  stacking mechanisms between  $\pi$ -acceptors in the functional amino group and N-heteroaromatic ring of SMX, and the  $\pi$ -donors within the carbon monoliths, as discussed in Chapter 10. Additionally, weak electrostatic attractions play a role in the adsorption

mechanisms, where the negatively charged SMX molecules interact with the positively charged surface of the carbon monoliths. Carrales-Alvarado et al. (2020) investigated the effect of surface area in graphite and graphene-based materials on their adsorption capacity for metronidazole and trimethoprim. They observed a linear increase in adsorption capacity with surface area and conclude that  $\pi$ - $\pi$  dispersive interactions predominantly governed the adsorption mechanisms.

**Table 11.4.** Adsorption capacities of different materials for SMX in aqueous solutions.

| Adsorbents                                                                    | Adsorption capacity (mg/g) | Experimental conditions  | Reference                     |
|-------------------------------------------------------------------------------|----------------------------|--------------------------|-------------------------------|
| ZnCl <sub>2</sub> -modified biochar                                           | 597.6                      | pH = 7, T = 25 °C        | Hou et al. (2023)             |
| <b>H<sub>2</sub>O-activated 3D-printed carbon monolith</b>                    | <b>488.6</b>               | <b>pH = 7, T = 25 °C</b> | <b>This work</b>              |
| Granular activated carbon F400                                                | 400.0                      | pH = 3, T = 25 °C        | Moral-Rodríguez et al. (2016) |
| Biochar derived from sugarcane bagasse                                        | 400.0                      | pH = 5.4, T = 30 °C      | Prasannamedha et al. (2021)   |
| <b>CO<sub>2</sub>-activated 3D-printed carbon monolith</b>                    | <b>379.1</b>               | <b>pH = 7, T = 25 °C</b> | <b>This work</b>              |
| Ordered mesoporous carbon                                                     | 334.0                      | pH = 4.5, T = 25 °C      | Sarker et al. (2023)          |
| Biochar derived from microalgal residues                                      | 287.9                      | pH = 4, T = 25 °C        | Tan et al. (2022)             |
| Fe-impregnated graphited biochar                                              | 187.3                      | pH = 5, T = 25 °C        | Zhang et al. (2020)           |
| Hexadecyltrimethylammonium bromide-modified organobentonite                   | 111.4                      | pH = 7, T = 25 °C        | Chapter 8 of this thesis      |
| Magnetic activated carbon nanocomposite                                       | 72.4                       | pH = 4, T = 35 °C        | Ghate et al. (2021)           |
| Non-activated 3D-printed carbon monolith                                      | 52.7                       | pH = 7, T = 25 °C        | This work                     |
| Powdered activated carbon embedded chitosan-polyvinyl alcohol composite beads | 9.1                        | pH = 4, T = 25 °C        | Zhou et al. (2020)            |
| Raw Ca-bentonite                                                              | 4.4                        | pH = 7, T = 25 °C        | Chapter 8 of this thesis      |



**Figure 11.9.** Effect of burn-off degree (a),  $S_{BET}$  (b) and  $V_{mic}$  on the uptake of SMX adsorbed  $Q_{100}$  on 3D-printed monolithic activated carbons.

### 11.3.3 Breakthrough curves of SMX on the 3D-printed monolithic activated carbons

To evaluate the dynamic performance of SMX adsorption on 3D-printed monolithic activated carbons, breakthrough curves were employed to investigate the impact of different activating agents and activation times. The experiments focused on monoliths equipped with interconnected network channels, maintaining constant operational parameters:  $Q = 0.58$  mL/min,  $C_{A0} = 50$  mg/L, pH = 7 and  $T = 25$  °C.

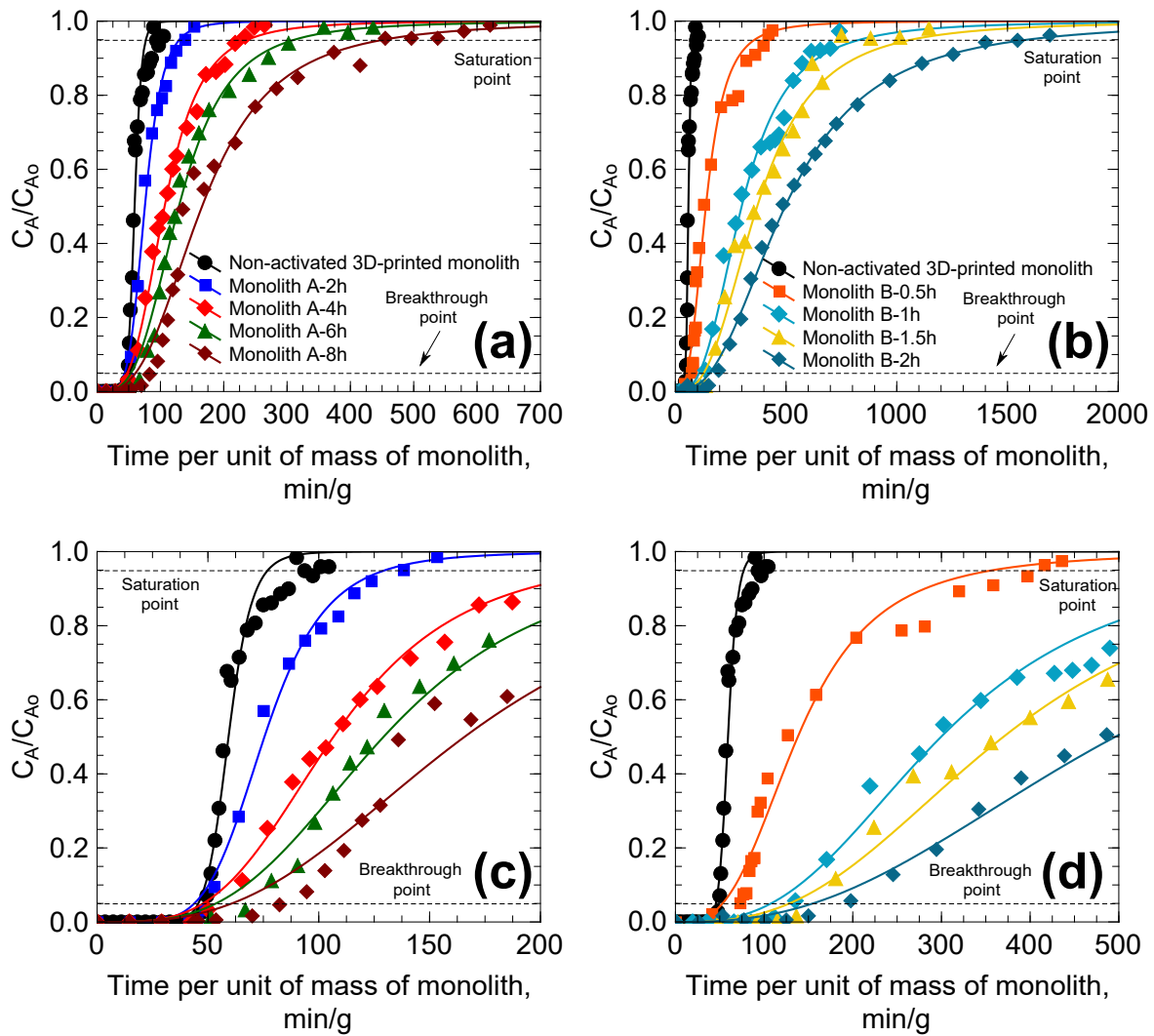
Various key parameters including adsorption capacity, breakthrough time, treated volume, mass transfer zone and the displacement rate of the mass transfer zone were analyzed to characterize the dynamic adsorption behavior. Equations (10.3-10.6) were applied for accurate estimation and interpretation of these parameters considering that the breakthrough point was defined at  $C_A/C_{A0} = 0.05$  and the saturation point at  $C_A/C_{A0} = 0.95$ .

The dynamic breakthrough curves for SMX adsorption on the 3D-printed monolithic activated carbons are illustrated in Figure 11.10. Figure 11.10 (a) depicts the effect of CO<sub>2</sub> activation on the breakthrough curves, while Figure 11.10 (b) shows the effect of H<sub>2</sub>O activation. Analyzing both sets of curves reveals a sigmoidal shape, which becomes progressively delayed in time and asymmetrical with longer activation periods for both activating agents, exhibiting fronting and tailing effects (Yin et al., 2019). Fronting refers to the early appearance of contaminant in the effluent, whereas tailing describes the gradual approach of the effluent towards the influent concentration, nearing column saturation.

To interpret these asymmetries in the breakthrough curves, a modified Bohart-Adams-Hutchins model was developed by Apiratikul and Chu (2021). This model defines a new set of parameters and variables equal to unity and reintroduces them into the BDST model, transforming them into logarithmic terms. The modified BDST model is represented by the following equation:

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + e^{k \ln\left(\frac{N_0 L}{U}\right) - k \ln(C_{A0} t)}} \quad (11.11)$$

The lines in Figure 11.10 represent the fits of the modified BDST model to the experimental data. The estimated fit parameters and the average percentage deviations are listed in Table 11.5, showing average deviation percentages below 10 % in most cases. This demonstrates the effectiveness of the modified BDST model in accurately describing the breakthrough behavior of SMX adsorption on the 3D-printed monolithic activated carbons.



**Figure 11.10.** Breakthrough curves for SMX adsorption on 3D-printed monolithic activated carbons from CO<sub>2</sub> (a) and H<sub>2</sub>O (b) at  $Q = 0.58$  mL/min,  $C_{A0} = 50$  mg/L, pH = 7 and  $T = 25$  °C. The figure includes an enlargement of the breakthrough curves for shorter time periods (c, d). The lines represent the modified BDST model.

Figures 11.10 (a) and 11.10 (b) demonstrate the significant impact of the activating agents and times on the breakthrough times, with these times progressively delayed as activation time increases. This trend highlights the importance of pore development on the dynamic adsorption performance. Figures 11.10 (c) and 11.10 (d) provide an enlarged view of the breakthrough curves for shorter time periods, which

better illustrates the effect of increasing breakthrough time per unit mass of the monoliths as the activation time rises, having a more pronounced effect for the H<sub>2</sub>O-activated 3D-printed monoliths. According to Table 11.5, the adsorption capacities at the breakthrough point increase with activation time. For the CO<sub>2</sub>-activated 3D-printed carbon monoliths, the maximum adsorption capacity was 2.34 mg/g in the Monolith A-8h sample. Conversely, for the H<sub>2</sub>O-activated 3D-printed monoliths, the adsorption capacity reached a maximum value of 5.46 mg/g in the Monolith B-2h sample, which is 2.3-fold higher than that of the Monolith A-8h sample.

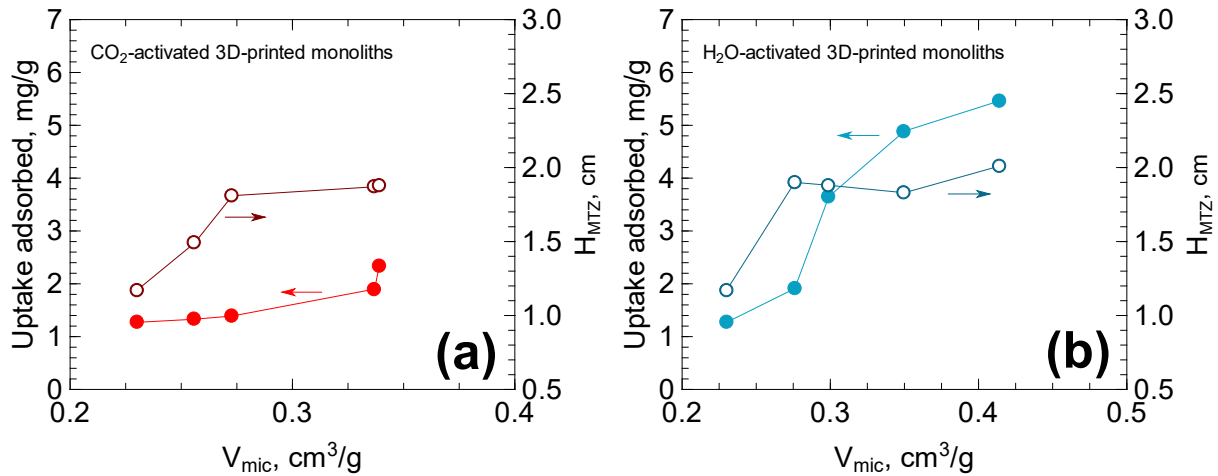
**Table 11.5.** Parameters of breakthrough curve experiments for SMX adsorption on 3D-printed monolithic activated carbons at  $Q = 0.58$  mL/min,  $C_{A0} = 50$  mg/L, pH = 7 and  $T = 25$  °C.

| Exp. No. | Monoliths              | k (L/min mg) | N <sub>0</sub> (mg/L) | %D <sub>BC</sub> | t <sub>b</sub> (min) | t <sub>s</sub> (min) | q <sub>b</sub> (mg/g) | q <sub>s</sub> (mg/g) | V <sub>b</sub> (mL) | V <sub>s</sub> (mL) | H <sub>MTZ</sub> (cm) | R <sub>MTZ</sub> (cm/h) |
|----------|------------------------|--------------|-----------------------|------------------|----------------------|----------------------|-----------------------|-----------------------|---------------------|---------------------|-----------------------|-------------------------|
| 1        | Non-activated monolith | 11.256       | 682.1                 | 9.5              | 68                   | 138                  | 1.27                  | 1.30                  | 39                  | 80                  | 1.17                  | 1.000                   |
| 2        | Monolith A-2h          | 5.419        | 823.2                 | 3.5              | 65                   | 107                  | 1.33                  | 1.71                  | 38                  | 107                 | 1.49                  | 0.744                   |
| 3        | Monolith A-4h          | 3.671        | 1136.7                | 9.4              | 65                   | 306                  | 1.39                  | 2.60                  | 38                  | 177                 | 1.81                  | 0.452                   |
| 4        | Monolith A-6h          | 3.347        | 1389.8                | 4.0              | 85                   | 456                  | 1.90                  | 3.44                  | 50                  | 264                 | 1.87                  | 0.303                   |
| 5        | Monolith A-8h          | 2.935        | 1699.1                | 7.7              | 100                  | 556                  | 2.34                  | 4.75                  | 58                  | 322                 | 1.88                  | 0.248                   |
| 6        | Monolith B-0.5h        | 3.087        | 1762.3                | 9.8              | 113                  | 646                  | 1.91                  | 3.05                  | 65                  | 374                 | 1.90                  | 0.214                   |
| 7        | Monolith B-1h          | 2.880        | 3503.7                | 5.6              | 195                  | 1066                 | 3.65                  | 7.06                  | 113                 | 618                 | 1.88                  | 0.130                   |
| 8        | Monolith B-1.5h        | 2.785        | 3387.8                | 6.5              | 205                  | 1006                 | 4.89                  | 10.67                 | 119                 | 583                 | 1.83                  | 0.137                   |
| 9        | Monolith B-2h          | 2.531        | 4140.2                | 5.9              | 205                  | 1606                 | 5.46                  | 16.34                 | 119                 | 931                 | 2.01                  | 0.086                   |

Figure 11.11 exhibits the variation of the uptake of SMX adsorbed at the breakthrough point and the mass transfer zone length as a function of  $V_{mic}$  for both CO<sub>2</sub> and H<sub>2</sub>O activations, illustrating the importance of pore development on dynamic adsorption performance. In Figure 11.11 (a), a slight increase in the uptake of SMX adsorbed at the breakthrough point is observed as  $V_{mic}$  increases. This result is attributed to the narrower micropores developed by CO<sub>2</sub> activation, which hinder SMX diffusion into the porosity. Despite the slight increase in adsorption capacity, there is a noticeable rise in H<sub>MTZ</sub> values with  $V_{mic}$ , indicating reduced efficiency of the bed utilization. This phenomenon is attributed to the reduction of mass transfer rates with



activation time, as evidenced by the asymmetries observed in the breakthrough curves (Fernández-Andrade et al., 2022).



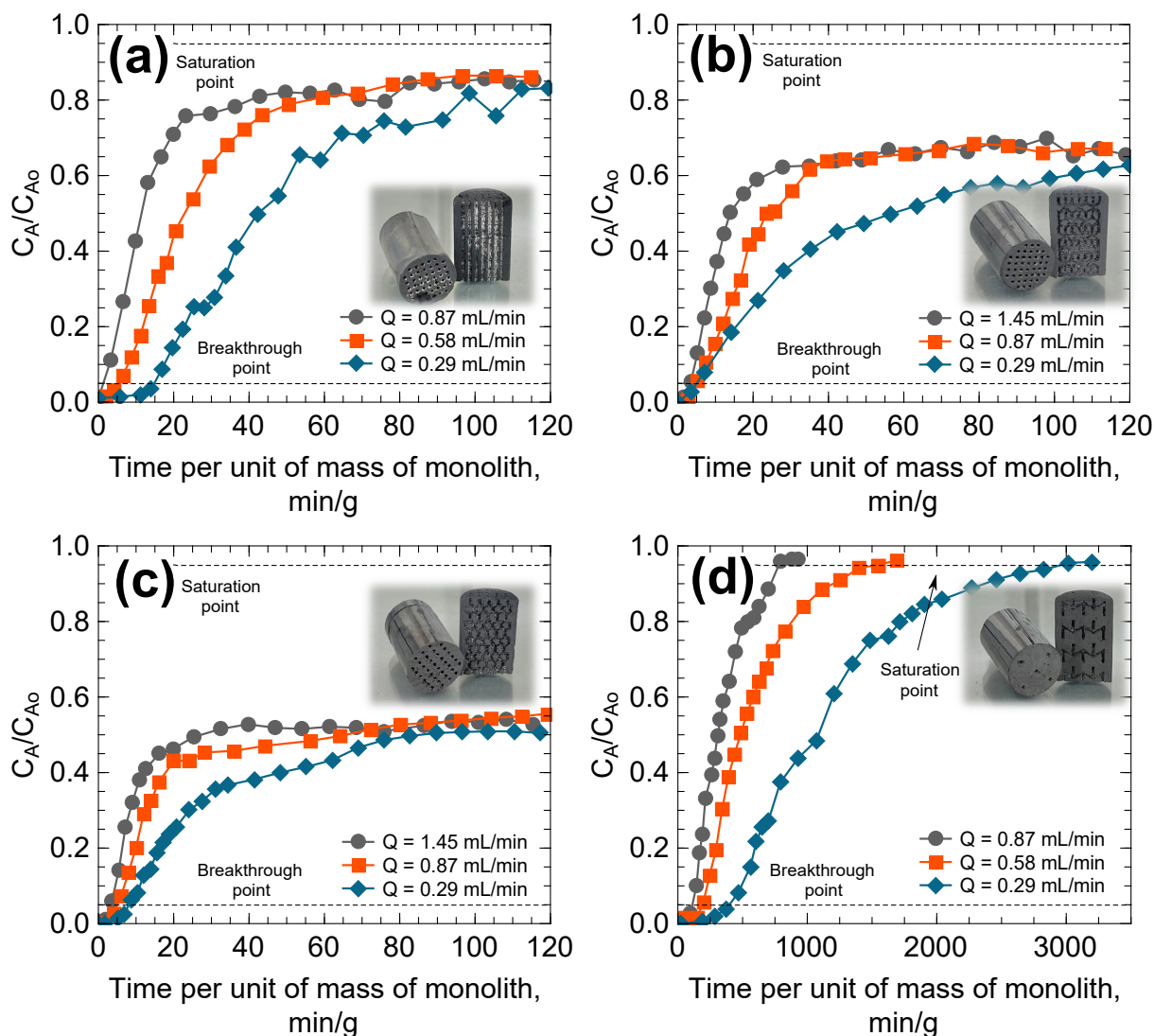
**Figure 11.11.** Variation of the uptake of SMX adsorbed at the breakthrough point and  $H_{MTZ}$  with  $V_{mic}$  for  $CO_2$  (a) and  $H_2O$  (b) activations.

For the  $H_2O$ -activated 3D-printed monoliths, Figure 11.11 (b) shows a dramatic increase in adsorption capacity as  $V_{mic}$  rises, contrasting with  $CO_2$ -activated monoliths. This enhancement can be explained by the more open porous texture that extends into the mesopore region, facilitating easier access of SMX to active sites across the monolithic structure. Although  $H_{MTZ}$  initially increases with  $V_{mic}$ , indicating mass transfer limitations, it remains constant as  $V_{mic}$  exceeds 0.276 cm<sup>3</sup>/g. This stability signifies that  $H_2O$  activation enhances adsorption capacity while maintaining reduced  $H_{MTZ}$  values and a relatively modest  $R_{MTZ}$ , leading to improved adsorption performance compared to  $CO_2$ -activated 3D-printed monoliths. These findings indicate promising potential for the large-scale application of  $H_2O$ -activated 3D-printed monoliths in adsorption processes.

#### 11.3.4 Effect of channel geometries of 3D-printed monoliths on dynamic SMX adsorption performance

The influence of different channel geometries on the dynamic adsorption performance of 3D-printed monolithic activated carbons was rigorously evaluated after

a 2-hour activation with H<sub>2</sub>O to ensure optimal performance. Four distinct prototypes of channel geometries were examined: straight, rhomboidal, hexagonal and interconnected network configurations. The breakthrough curves obtained at various volumetric flow rates are presented in Figure 11.12.



**Figure 11.12.** Effect of channel geometries on breakthrough curves for SMX adsorption on 3D-printed monolithic activated carbons at different volumetric flow rates (a-d),  $C_{A0} = 50$  mg/L, pH = 7 and T = 25 °C.

Figure 11.12 (a) displays the performance of the conventional straight channel geometry. Breakthrough occurred rapidly, within less than 20 min per gram of the

monolith, regardless of the volumetric flow rate. This rapid breakthrough is primarily attributed to channeling effects, where preferential pathways form along the monolith, limiting effective adsorption (Beckwée et al., 2022). Interestingly, the breakthrough curve did not reach the saturation point at  $C_A/C_{A0} = 0.95$ . Instead, the curves stabilized at  $C_A/C_{A0} = 0.85$ , irrespective of flow rates. This suggests that a significant portion of SMX molecules exited the column without being adsorbed. As time proceeds, mass transfer contributions become significant, leading to partial adsorption of molecules within the monolith while others exit unadsorbed. This phenomenon is due to the linear flow pattern imposed by the straight channel geometry, which limits interaction and diffusion between the liquid phase and the monolith.

The performance of the rhomboidal channel geometry is shown in Figure 11.12 (b). The tortuous path created by the rhomboidal channels did not fully resolve the rapid breakthrough observed at times less than 20 min/g. However, similar to the straight channel monolith, the curves did not reach the saturation point, stabilizing at  $C_A/C_{A0} = 0.65$  regardless of the volumetric flow rates, which is 23.5 % lower than the straight channel monolith. This indicates improved adsorption, with a greater portion of SMX molecules being adsorbed within the monolith and fewer exiting unadsorbed. The tortuous path created by the rhomboidal channels enhances mass transfer, reduces channeling effects and increases interaction between the liquid phase and the adsorbent, thus improving adsorption performance compared to the straight channel monoliths.

Figure 11.12 (c) illustrates the performance of the hexagonal channel geometry, which provides a tortuous path similar to the rhomboidal design but with a different structural arrangement. The breakthrough curves for this geometry at different volumetric flow rates also show rapid breakthrough at times less than 20 min/g. However, the hexagonal channels exhibited a stabilization point close to  $C_A/C_{A0} = 0.55$ , significantly lower than that of the straight and rhomboidal geometries. This behavior indicates a 35.3 % improvement in reducing channeling effects compared to the straight channel monolith and 15.4 % improvement over the rhomboidal channel geometry. The reduced channeling effects in the hexagonal design suggest better interaction and

diffusion between the liquid phase and the monolith, enhancing mass transfer and overall adsorption performance. The structural arrangement of hexagonal channels facilitates more efficient contact and diffusion of SMX molecules, resulting in superior dynamic adsorption behavior.

The breakthrough curves for the interconnected network channel design are shown in Figure 11.12 (d). This advanced geometry significantly enhances adsorption performance, evidenced by much longer breakthrough times compared to other geometries. Within the first 20 min/g, no breakthrough occurred regardless of the volumetric flow rates, indicating that channeling effects are effectively mitigated. The complex flow pattern induced by this geometry generates turbulence, enhancing diffusion throughout the monolith. This results significantly improved mass transfer and adsorption performance.

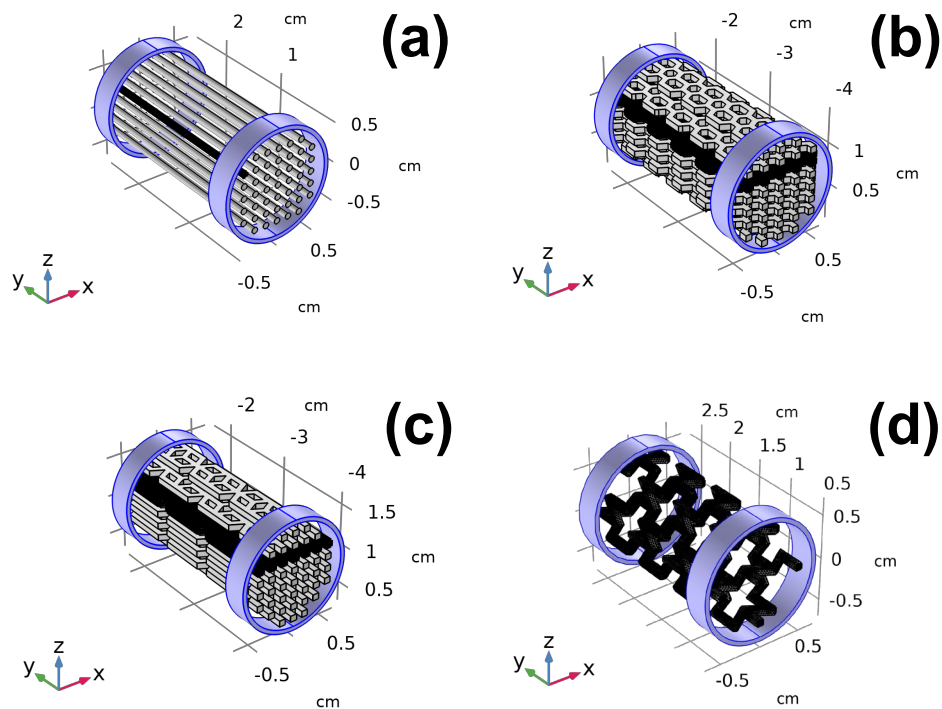
These findings highlight the ability of 3D printing technology to precisely control the channel geometries of monoliths, substantially enhancing adsorption efficiency. This technological advancement represents a significant leap in the design of packed bed columns for adsorption purposes, potentially revolutionizing the field with enhanced efficiency and effectiveness.

### **11.3.5 Computational Fluid Dynamics (CFD) on channel geometry prototypes**

The influence of channel geometry on breakthrough curves is undoubtedly shaped by the fluid hydrodynamics, as SMX follows distinct pathways within the monolithic adsorbent. To delve into the intricate fluid dynamics governing these sophisticated channel configurations, COMSOL Multiphysics was employed.

Geometry prototypes designed in SolidWorks were exported and imported into COMSOL Multiphysics. These prototypes were discretized into multiple subdomains, as depicted in Figure 11.13. In the case of the straight channel monolith (Figure 11.13 (a)), the grid mesh was constructed within a single channel, assuming that the mass and momentum balances within one channel could represent others due to their lack of interconnection. This grid mesh consisted of 62,643 domain elements, 320 contour elements and 4 corner elements. The rhomboidal and hexagonal geometries (Figures

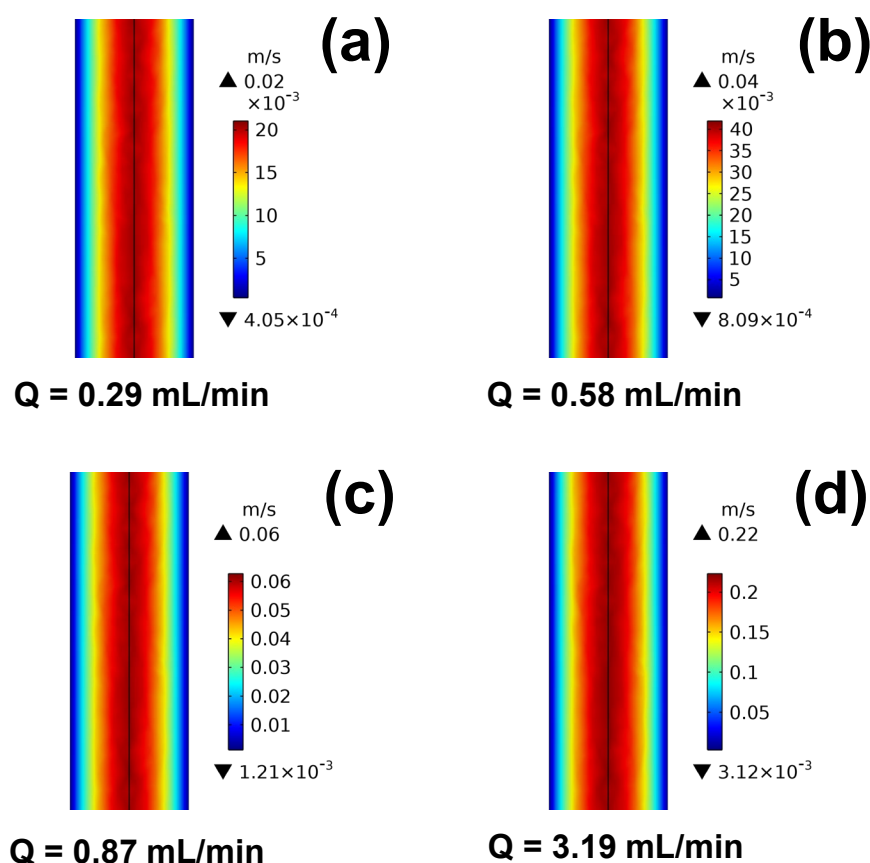
11.13 (b) and 11.13 (c)) consisted of layers exhibiting tortuous patterns along the monolith's length, where these layers are separated by carbon walls, as discussed in Section 11.2.1. Their grid meshes comprised 1,058,526 domain elements, 7,186 contour elements and 476 corner elements for the rhomboidal geometry and 2,796,440 domain elements, 14,860 contour elements and 882 corner elements for the hexagonal geometry. For the interconnected network channel geometry, the grid mesh was more complex, totaling 580,281 domain elements, 9,082 contour elements and 826 corner elements.



**Figure 11.13.** Visualization of the channel geometry prototypes (a-d) imported into COMSOL Multiphysics and the corresponding domain grid mesh.

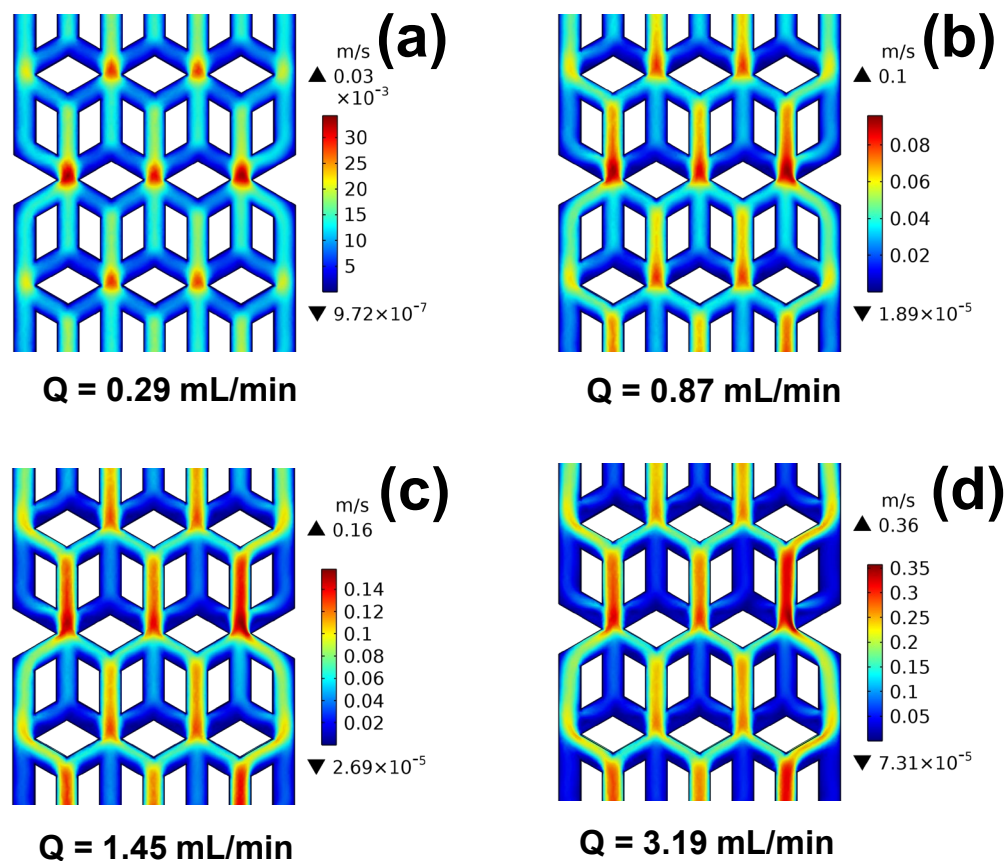
The model was solved under turbulent conditions using the  $\kappa$ - $\epsilon$  turbulence model, which incorporates Navier-Stokes equation, continuity equation, turbulence kinetic energy balance and turbulence dissipation rate balance. Once the mathematical model was programmed, COMSOL calculated the hydrodynamics across all channel geometries.

Figure 11.14 depicts the velocity profiles of SMX within the straight channel configuration at varying volumetric flow rates of 0.29, 0.58, 0.87 and 3.19 mL/min. As expected, regardless of the volumetric flow rate, the fluid consistently formed a typical parabolic velocity profile from the entrance to the exit of the channel. Turbulence did not develop inside the channel; instead, preferential pathways with uniform laminar flow were established along the length of the monolith. This laminar flow pattern restricts adsorbate-adsorbent interaction, thereby impeding the diffusion of SMX within the porous structure of the monolithic adsorbent, which aligns with the early breakthrough observed experimentally. The maximum velocities registered were 0.02, 0.04, 0.06 and 0.22 m/s at the center of the channel for volumetric flow rates of 0.29, 0.58, 0.87 and 3.19 mL/min, respectively.



**Figure 11.14.** Velocity profiles of SMX within the straight channel geometry at volumetric flow rates of 0.29 (a), 0.58 (b), 0.87 (c) and 3.19 mL/min (d).

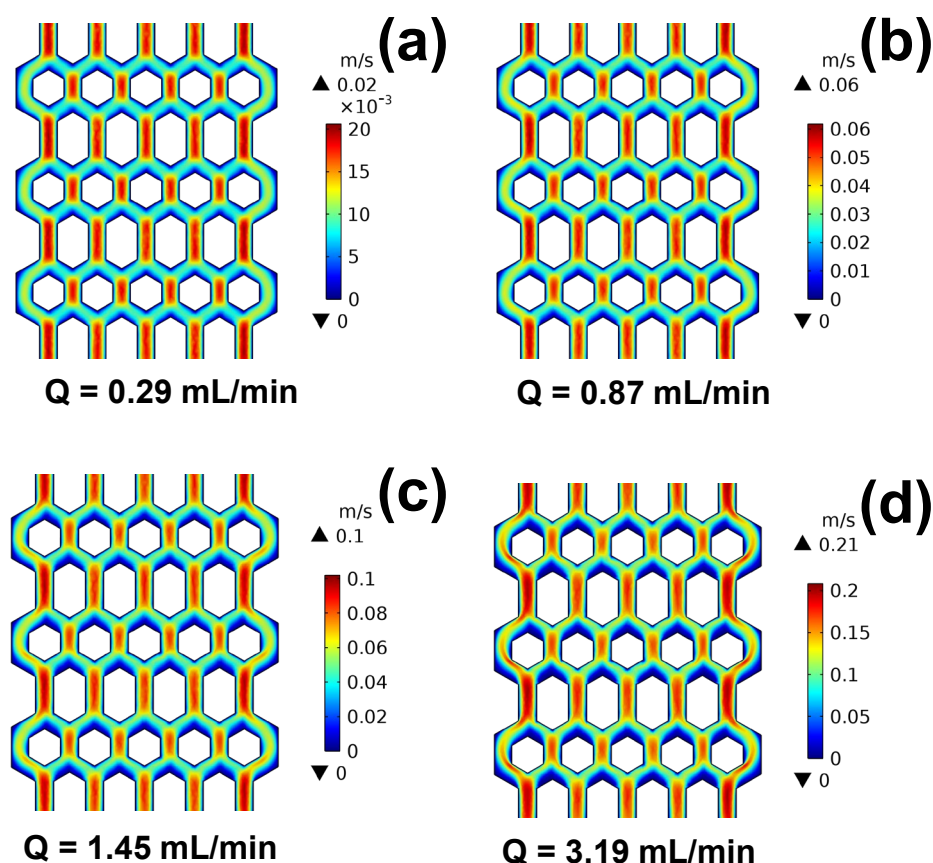
Figure 11.15 shows the velocity profiles of SMX within the rhomboidal channel geometry at different volumetric flow rates. In this geometry, fluid flows in a tortuous rhomboidal path along the monolith. As the volumetric flow rates increase, preferential flow paths with a hexagonal shape become evident, generating dead zones inside the monolith. These dead zones limit the effective distribution of the fluid along the monolith, as not all channels are utilized, leading to a heterogeneous fluid distribution. This limitation can negatively impact adsorption performance, as the interaction between the adsorbate and the adsorbent is restricted. The maximum velocities recorded were 0.03, 0.1, 0.16 and 0.36 m/ for volumetric flow rates of 0.29, 0.58, 0.87 and 3.19 mL/min, respectively.



**Figure 11.15.** Velocity profiles of SMX within the rhomboidal channel geometry at volumetric flow rates of 0.29 (a), 0.87 (b), 1.45 (c) and 3.19 mL/min (d).



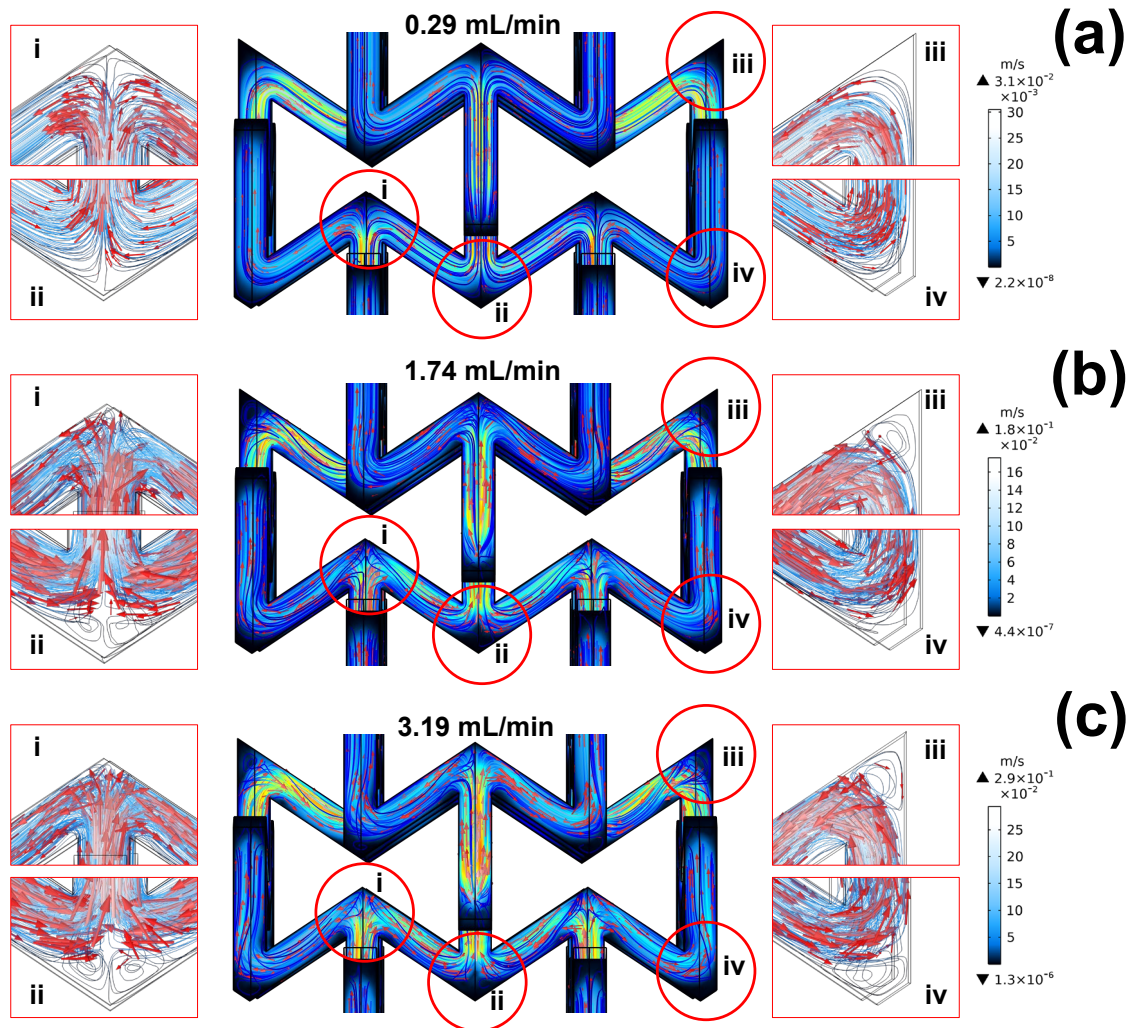
The velocity profiles of the hexagonal geometry are illustrated in Figure 11.16. In this geometry, fluid follows a more tortuous path along the monolith, with pathways intertwining to ensure better fluid distribution within the monolith. Compared to the rhomboidal monolith, preferential flow paths are not formed as the volumetric flow rates increase. Instead, a more homogeneous fluid distribution is developed, ensuring optimal usage of the entire monolith. This improved distribution results in better adsorption performance, as observed in the breakthrough curves compared to the rhomboidal channel monolith. The maximum velocities found in the monolith were 0.02, 0.06, 0.1 and 0.21 m/s for volumetric flow rates of 0.29, 0.58, 0.87 and 3.19 mL/min, respectively, which are relatively lower than those in the rhomboidal channels.



**Figure 11.16.** Velocity profiles of SMX within the hexagonal channel geometry at volumetric flow rates of 0.29 (a), 0.87 (b), 1.45 (c) and 3.19 mL/min (d).



Figure 11.17 presents the velocity profiles within the interconnected network channels at volumetric flow rates of 0.29, 1.74 and 3.19 mL/min. The complex channel structure was intentionally designed with four distinct zones, termed “collision zones”, strategically positioned along its length. An enlarged depiction of each collision zone is provided to enhance clarity regarding the velocity profiles.



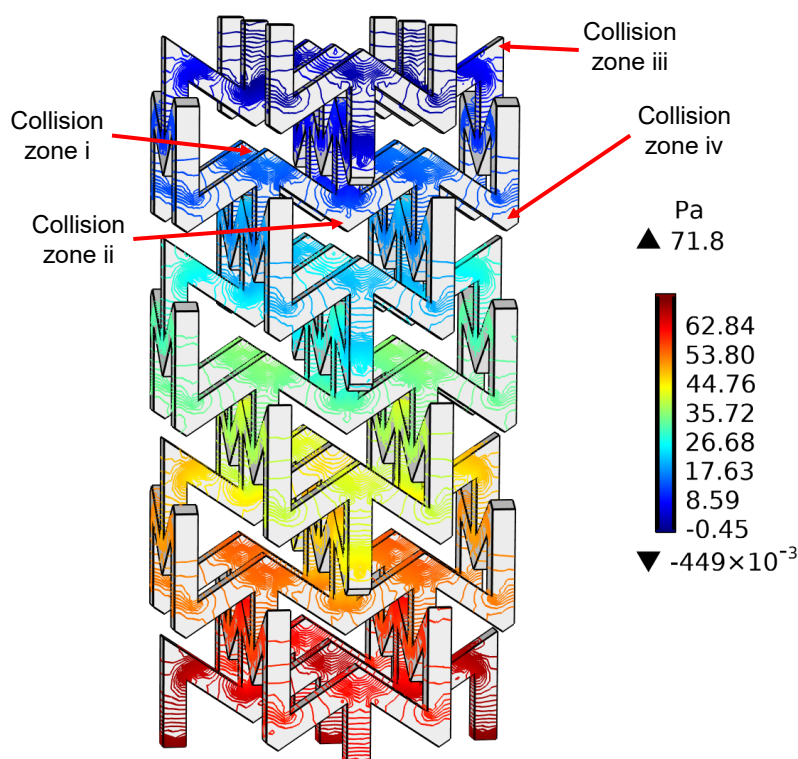
**Figure 11.17.** Velocity profiles of SMX within the interconnected network channel geometry at volumetric flow rates of 0.29 (a), 1.74 (b) and 3.19 mL/min (c).

In zone i, the fluid is intentionally directed to impact directly against the carbon wall, resulting in a bifurcation into two streams propagating radially. Moving to zone ii,

the fluid is directed into a mixing zone, where it interacts with fluid from another stream before being redirected to a zone of direct impingement against the carbon wall once again. Zones iii and iv are positioned at the edges of the monolith, where fluid from both axial and radial streams converges to impact directly against the outer wall of the carbon monolith. This deliberate arrangement ensures thorough distribution, mixing and interaction of the fluid within the monolithic structure.

Turbulence is evident within the monolith regardless of the volumetric flow rate, becoming more pronounced as the volumetric flow rate increases. At 0.29 mL/min, the fluid flows in a disordered turbulent regime across all four zones. When the flow rate increases to 1.74 mL/min, eddy zones with low velocities ( $< 0.02$  m/s) become apparent in collision zones ii and iii, indicating a more complex and disordered fluid flow. At 3.19 mL/min, the turbulent flow transitions to a more chaotic state, forming large eddies with low velocities (less than 0.05 m/s) in zones ii, iii and iv, accompanied by uncontrolled impacts occurring in zone i. The significant reduction in velocity within the collision zones enhances diffusion to the carbon walls. This complex geometry of channels within the monolithic structure promotes efficient mass transfer of SMX to the designed carbon structure, thereby enhancing adsorption efficiency. This improvement is corroborated by the extended breakthrough times observed experimentally.

The pressure profiles of the interconnected network channel geometry at a volumetric flow rate of 0.29 mL/min are depicted in Figure 11.18. Significant differences in pressure gradients are observed along the monolith, decreasing gradually as fluid travels from the entrance at the bottom to the exit at the top. The maximum pressure gradient registered was 71.8 Pa at the entrance of the monolith. Notably, major pressure gradients were observed in zones i and iii, which are associated with the fluid's direct impingement against the carbon wall, increasing pressure. In contrast, zones ii and iv registered lower pressure gradients due to the absence of direct impingement against the monolith. The connecting zones between each collision zone showed a more uniform pressure distribution.



**Figure 11.18.** Pressure profiles within the interconnected network channel geometry at a volumetric flow rate of 0.29 mL/min.

## 11.4 Conclusions

3D-printed monolithic activated carbons from CO<sub>2</sub> and H<sub>2</sub>O were synthesized using an innovative method that combines sol-gel polymerization with advanced 3D printing technology. Four distinct channel geometries, including straight, rhomboidal, hexagonal and interconnected network were meticulously designed using CAD software and fabricated to target the removal of SMX from water.

The manufactured monoliths exhibited excellent replication of the original CAD designs, demonstrating high fidelity to the original 3D prototypes. This precise structural control was crucial for optimizing fluid dynamics and enhancing adsorption performance.

Morphological analysis revealed that the monoliths consisted of uniformly sized spherical primary particles, forming a robust macrostructure with reduced flow resistance. Both H<sub>2</sub>O and CO<sub>2</sub> activation processes effectively removed residual

carbon deposits from the channel surfaces, which were remnants of the 3D template used during carbonization. This process mitigated macropore blockage issues and developed a wider porosity, resulting in significantly increasing  $S_{\text{BET}}$  values exceeding  $1000 \text{ m}^2/\text{g}$ .

$\text{CO}_2$  activation led to gradual enlargement of pores within the micropore region, whereas  $\text{H}_2\text{O}$  activation created larger pores, shifting the pore distribution towards the narrow mesopore region. This differentiation in pore development was instrumental in enhancing the adsorption capacity and efficiency of the monoliths.

Adsorption isotherms revealed that the adsorption capacity for SMX increased drastically with activation time for both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The maximum adsorption capacities were  $379.1 \text{ mg/g}$  for the 8-hour  $\text{CO}_2$ -activated monolith and  $488.6 \text{ mg/g}$  for the 2-hour  $\text{H}_2\text{O}$ -activated monolith, surpassing most values reported in the literature for other adsorbents. The linear increase in adsorption capacity with  $S_{\text{BET}}$  and  $V_{\text{mic}}$  values demonstrated that  $\pi$ - $\pi$  dispersive interactions predominantly governed the adsorption mechanisms.

Breakthrough curves showed that activation time and agent significantly affected performance. The breakthrough time increased with longer activation times for both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , though an asymmetrical sigmoidal breakthrough developed due to higher  $H_{\text{MTZ}}$  values, indicative of reduced mass transfer rates. Compared to  $\text{CO}_2$ -activated monoliths,  $\text{H}_2\text{O}$ -activated monoliths exhibited higher adsorption capacity due to a more open porous texture extending into the mesopore region, improving SMX accessibility.

Channel geometry strongly impacted breakthrough curves. Conventional, rhomboidal and hexagonal geometries experienced rapid breakthrough due to channeling effects, where preferential pathways limited effective adsorption. However, the interconnected network channel design significantly enhanced adsorption performance, evidenced by much longer breakthrough times and effectively mitigated channeling effects. The complex flow patterns induced by this geometry generated turbulence, enhancing diffusion throughout the monolith, as confirmed by CFD simulations. This significantly improved mass transfer and adsorption performance.

# CHAPTER

GENERAL CONCLUSIONS

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The adsorption capacity of raw clays for TC, TMP and CPA is significantly influenced by their structural arrangement, swelling capability, interlayer cation nature and the molecular size of the pharmaceuticals. Among the studied clays, bentonite exhibited the highest adsorption capacities: 283.5 mg/g for TC, 186.6 mg/g for TMP and 159.8 mg/g CPA. Adsorption on bentonite occurred on the external surface and within the interlayer spaces, driven by cation exchange and electrostatic attractions. The molecular size of the pharmaceuticals and the swelling capacity of bentonite were crucial, with larger molecules leading to increased  $d_{001}$  values. Bentonite maintained over 85 % adsorption efficiency after five reuse cycles.

The adsorption kinetics of TMP, TC and CPA on bentonite were analyzed using the EMTM and PVSDM diffusion models. The EMTM model did not fit the experimental data, indicating that external mass transfer does not affect the adsorption rate. The PVSDM model provided a good fit, showing that TMP and TC adsorption rates were influenced by surface and pore volume diffusion, with increasing  $D_{e,s}$  values corresponding to higher adsorption capacities. For CPA, adsorption was controlled by pore volume diffusion alone, estimating an experimental tortuosity factor of 9.64. Intraparticle diffusion mechanisms varied with adsorption capacity, leading to increased surface diffusion as adsorption capacity rose.

The binary adsorption of TC and Cd(II) on bentonite was pH-dependent. At pH = 3, a competitive effect was observed as both contaminants competed for the same cationic sites on the negatively charged surface of bentonite. At pH = 7, a cooperative effect was evident, with adsorption occurring through complexation mechanisms.

Hexadecyltrimethylammonium bromide-modified organobentonite was synthesized successfully, with the surfactant intercalated within the interlayer space, forming a double layer of molecules. This modification increased the basal spacing (001) from 1.50 to 1.94 nm and changed the surface charge from negative and hydrophilic to positive, hydrophobic and organophilic.

Adsorption isotherms revealed distinctive capacities for CPA, TC, SMX and CBZ on both unmodified bentonite and organobentonite. Bentonite had higher capacities for CPA (147.6 mg/g) and TC (188.3 mg/g), but lower for SMX (113.1 mg/g) and CBZ (47.5

mg/g). Conversely, organobentonite showed elevated capacities for TC (177.0 mg/g), SMX (113.1 mg/g) and CBZ (47.5 mg/g), but lower for CPA (9.8 mg/g). These results highlight the influence of the ionic charge of the pharmaceutical compound and the surface charge of the adsorbent on adsorption capacities, with electrostatic attractions and hydrophobic partitioning playing key roles.

Innovative 3D-printed carbon monolith adsorbents with varied channel geometries and porous textures were fabricated using sol-gel polymerization and 3D printing technology. The resorcinol/catalyst ratio (R/Cs), activating agent (CO<sub>2</sub> and H<sub>2</sub>O), activation times and channel geometries were optimized for SMX removal from water. Four distinct channel geometries: straight, rhomboidal, hexagonal and interconnected network were designed and printed accurately.

The carbon monolithic structures exhibited optimal integration, structural integrity and excellent replication of the original designs. Higher R/Cs ratios resulted in larger spherical primary particles, creating a hierarchical porous structure with reduced flow resistance and modulating pore diameter and skeleton size within the macropore range (95.1 to 157.1 nm). Both H<sub>2</sub>O and CO<sub>2</sub> activation effectively removed residual carbon deposits, developing wider porosity and resulting in  $S_{\text{BET}}$  values exceeding 1000 m<sup>2</sup>/g. CO<sub>2</sub> activation enlarged micropores, while H<sub>2</sub>O activation created larger mesopores.

Adsorption isotherms showed that SMX adsorption capacity increased with activation time for both CO<sub>2</sub> and H<sub>2</sub>O. The maximum adsorption capacities were 379.1 mg/g for the 8-hour CO<sub>2</sub>-activated monolith and 488.6 mg/g for the 2-hour H<sub>2</sub>O-activated monolith, with adsorption governed by  $\pi$ - $\pi$  dispersive interactions.

Breakthrough curves indicated that activation time and agent significantly affected performance. Longer activation times increased breakthrough time, with asymmetrical sigmoidal curves indicating reduced mass transfer rates. H<sub>2</sub>O-activated monoliths had higher adsorption capacities due to a more open porous texture, improving SMX accessibility. Channel geometry significantly impacted performance. The interconnected network channel design enhanced adsorption by generating turbulence and mixing, improving diffusion.

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