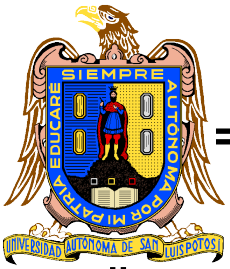

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FACULTAD DE CIENCIAS QUÍMICAS

POSGRADO EN CIENCIAS EN INGENIERÍA QUÍMICA

“Síntesis, caracterización y evaluación de propiedades de polímeros de base biológica de ácido acrílico-*Schizochytrium* sp.”

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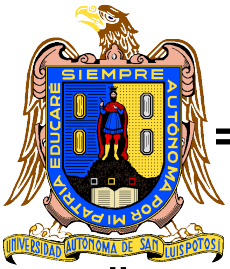

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GRADUATE OF CHEMICAL ENGINEERING SCIENCES

"Synthesis, characterization and evaluation of the properties of acrylic acid-*Schizochytrium* sp. bio-based polymers"

A THESIS FOR THE DEGREE OF:

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En el año 2006, justo cuando estaba en la preparatoria, descubrí mi gusto por la ciencia y la química, pero jamás imaginé que esa curiosidad se convertiría en pasión y que llegaría a este momento.

El camino nunca fue fácil, las horas de trabajo, el tiempo dedicado a la escritura y al análisis; el estrés generado, los cambios emocionales, los problemas de salud, las dificultades financieras, entre otras cosas; no podrán igualar las horas de amor, alegría y satisfacción de todos estos años.

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RESUMEN

Se estudiaron dos polímeros a base de ácido acrílico. El primero fue un poli(ácido acrílico-co-ácido itacónico)/NaOH, un hidrogel sintético, sintetizado con el propósito de conocer su capacidad de hinchamiento y su capacidad para eliminar óxido de hierro y cobre de superficies metálicas. Se demostró que la formación del copolímero y la neutralización de los grupos carboxílico mejoraron la capacidad de eliminación de óxido y su capacidad de hinchamiento. La remoción máxima de óxido de hierro fue de 269 mg g^{-1} de hidrogel, valor cuatro veces mayor que el reportado en la literatura. El segundo hidrogel fue un polímero innovador de base biológica de ácido acrílico y *Schizochytrium* sp. realizado por primera vez. La célula completa de *Schizochytrium* sp. (SCZ) y su fracción celular insoluble (FIP) se utilizaron como precursores para la polimerización. Se realizaron espectroscopía infrarroja (FTIR), termogravimetría (TGA) y microscopía electrónica de barrido (SEM) para determinar la formación del copolímero, las propiedades térmicas y su morfología. Las propiedades térmicas y mecánicas de los nuevos hidrogeles híbridos dependieron del tipo y concentración de la biomasa de microalgas. La temperatura de transición vítrea (T_g) de los biopolímeros disminuyó al aumentar el porcentaje de *Schizochytrium* sp., mientras que ocurrió lo contrario para el polímero con FIP. La resistencia mecánica máxima de los biopolímeros fue del 715% de elongación y se encontró a 50 ºC. El alargamiento del polímero de base biológica aumentó de 2 a 7 veces al aumentar la concentración de biomasa de microalgas. La flexibilidad aumentó de 3 a 4 veces cuando se utilizó su pared celular insoluble en lugar de la célula completa. Una evaluación hidrolítica reveló la capacidad máxima de hinchamiento (30000%) cuando se expone a condiciones fisiológicas (pH 7,4). En términos de sus propiedades, estos polímeros de base biológica pueden ser adecuados para aplicaciones biológicas y ambientales.

Palabras clave: biopolímero; hidrogel; microalgas; poli(ácido acrílico); *Schizochytrium*

ABSTRACT

Two polymers based on acrylic acid were studied. The first one was a poly(acrylic acid-co-itaconic acid)/NaOH, a synthetic hydrogel, synthetized with the purpose to discover its swelling capacity and its ability to remove iron and copper rust from metallic surfaces. It was proven that copolymer formation and neutralization of carboxylic acid groups highly improved the rust removal capabilities and its swelling ability. The maximum iron rust removal was 269 mg g^{-1} of hydrogel, a value which is four times greater than that reported in literature. The second hydrogel was an innovative bio-based polymer of acrylic acid and *Schizochytrium* sp. performed for the first time. The whole cell of *Schizochytrium* sp. (SCZ) and its insoluble cell fraction (FIP) were used as precursors for the polymerization. Infrared spectroscopy (FTIR), thermogravimetry (TGA), and scanning electron microscopy (SEM) were performed to determine the copolymer formation, the thermal properties, and its morphology. The new hybrid hydrogels' thermal and mechanical properties were dependent on the microalgae biomass type and concentration. The temperature of glass transition (T_g) of the biopolymers decreased when increasing *Schizochytrium* sp. percentage, while the opposite occurred for polymer with FIP. The maximum mechanical strength of the biopolymers was 750 % of elongation and was found at 50 ºC. The elongation of the bio-based polymer raised 2–7 times upon increasing the microalgal biomass concentration. Flexibility increased 3–4 fold when using its insoluble cell wall instead of whole cell. A hydrolytic assessment revealed the maximum swelling capacity (30000 %) when exposed to physiological conditions (pH 7.4). In terms of their properties, these bio-based polymers can be suitable for biological and environmental applications.

Keywords: biopolymer; hydrogel; microalgae; poly(acrylic acid); *Schizochytrium*

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CHAPTER 1. GENERAL INTRODUCTION

Polymers arise from a reaction called polymerization, which is a chemical process in which small molecules (monomers) are chemically grouped, giving rise to a high molecular weight molecule. These polymers have many desirable characteristics such as high mechanical resistance, long lifespan, low price, resistance to humidity, good electrical and thermal insulating properties, and they are recyclable. However, despite their great utility and advantages, they are flammable, expensive to recycle, and their durability makes it tough to biodegrade (they take up to 100 years to degrade) [1,2] causing accumulation in the environment.

A solution to this problem is to use polymers from living beings, called biopolymers. These materials could be natural or synthetic. Naturals produced from renewable sources have high biocompatible and biodegradable properties. However, their preparation costs are high, and their mechanical properties are usually weak. The synthetics have the particular advantage of being prepared according to customer demand, having the option of deciding the functional groups and molecular weights required for a given application, but they are not biodegradable. Currently, various hybrid materials with biodegradable, biocompatible, and mechanical properties of both are studied to reduce the environmental contamination produced by these polymers and avoid the loss of mechanical properties that are conducive to biomedical and environmental applications, replacing the materials most used today.

In this context, the research in this paper focuses on the synthesis and study of physicochemical, thermal, and mechanical properties of a new copolymer synthesized from acrylic acid and the microalgae *Schizochytrium* sp. The goal was to obtain a biopolymer with modulable properties of swelling, elasticity, mechanical, and thermal resistance; as well as biodegradable/biocompatible characteristics.

1.1 Biopolymers

According to the degradation properties, biopolymers can be classified as biodegradable and non-biodegradable [1]. Non-biodegradable ones are commonly used in medicine for their inert capacity, examples include polyethylenes, polyacrylates, polypropylenes, polyamides (nylons), polyurethanes and polysiloxanes (silicones). Applications include coatings on devices (eg, improving blood compatibility), implantable drug delivery systems, artificial hearts, implants (eg, nails, screws, bone plates), catheters and tubes for dialysis, etc.

The applications of biodegradable synthetic polymers can be found in tissue engineering, temporal structures, regenerative medicine, or in the controlled release of genes or drugs.

Biodegradable synthetic polymers such as poly (glycolic acid), poly (lactic acid) and their copolymers, and copolymers of trimethyl carbonate and glucolloids have been used for a number of clinical applications. The most frequently mentioned include resorbable sutures, drug delivery systems, and orthopedic fixation of nails, threads, and screws.

1.1.1 Biodegradable biopolymers

Biodegradable polymers offer a number of advantages over other materials because they provide the ability to improve mechanical properties and degradation kinetics, moreover, they can be manufactured in various desirable pore shapes and morphologies for different applications.

Erosion is the key for the degradation process of polymers. There are two main ways in which polymeric bonds can be split: passively by hydrolysis or actively by enzymatic reaction [3]. The enzymatic reaction is only effective for natural biopolymers such as polysaccharides, proteins (gelatin and collagen) and poly (beta-hydroxy acids), where appropriate enzymes are available.

1.2 Natural polymers

The difference between synthetic and natural polymers is that the natural polymers are obtained mainly from plants, animals and microbial sources that are classified based on their chemistry into polysaccharides, proteins, polyesters and polyamides [1]. Their reactive chemical bonds provide an ease of biodegradability, which in turn makes them biocompatible. Furthermore, their desirable characteristics of abundance, biocompatibility and biodegradability make them potential materials for various uses. The favorable eco-friendliness of these polymers makes them attractive to researchers.

1.2.1 Algae and microalgae

Until a few years ago, algae was the buzzword in the biofuel industry. Today it is used for the animal feed industry. In addition, algae contribute to the air we breathe since they produce almost 50% of the oxygen in the atmosphere and directly supports ocean life, thus playing an important role in global productivity [4].

Additionally, algae can be considered to be of great interest from a nutritional point of view because it contains a high concentration of proteins, dietary fiber, lipids with a high concentration of omega-3 and omega-6 fatty acids, and a valuable source of vitamins and minerals [5].

A current trend towards bioactive natural products with applications in various industries, such as pharmaceutical, biomedical, cosmetic and food has placed some emphasis on research on marine organisms, including macroalgae and microalgae. These constitute a type of compounds that have already been shown to have several important properties, such as anticoagulant and/or antithrombotic, immunomodulatory capacity, antitumor and cancer preventative, antilipidemic and hypoglycemic, antibiotic, anti-inflammatory and also antioxidant [6]. These desirable properties promise bioactive products and biomaterials with a wide range of applications. Their properties are mainly due to their structure and the physicochemical characteristics, depending on the organism. Furthermore, in the biomedical field, algae polysaccharides can be used in controlled drug delivery, wound management, and regenerative medicine.

1.2.1.1 Current applications

In the last decade, extensive literature has been published on the benefits and uses of various polysaccharides of brown, red and green macroalgae when it comes to health, nutrition, or even as drug carrier. Comparatively, there are only a handful of research papers on microalgae [7–11], despite their rich composition and simplicity of growth.

On the other hand, algal biomass has been widely exploited as a commercial source of biofuels and accumulation of polyphosphates [12]. Yet, the remaining algae (rich in protein) from the biofuel industry continues to offer a great opportunity for its disposal and use.

Applications of algae on the environmental side have been to mitigate the polymerization of silica [13,14] and to absorb pollutants in water [15,16].

However, there are no previous works in the literature in which microalgae biomass is used as a nucleus for the synthesis of polymers and only Chahuan et al. [17] have reported a bio-inspired control of silica using dendrimers from microalgae.

1.2.2 *Schizochytrium* sp.

In particular, the microalgae *Schizochytrium* sp. produces compounds beneficial to human and animal health as some of its biomolecules have natural immunogenic properties that make them interesting for the production and delivery of recombinant vaccines.

The cell wall was chosen as the focus of this research since it is a residue from the food industries for the production of polyunsaturated fatty acids (PUFAs) and from the pharmaceutical industries that use them for various biomedical applications.

Darley et al. [18] showed that the chemical composition, structure, and synthesis method of *Schizochytrium* cell walls do not support its inclusion in the order *Saprolegniales* as had been thought. Instead, they discovered that galactose is the main monomer of cell walls, particularly in the L configuration (> 95%), also

separating it from the order *Oomycetes*. Since the cell wall of *Schizochytrium* has L-galactose in abundance, its most related order is found only among the *Rhodophyceae* (red seaweed). Furthermore, no further works on the cell wall of *Schizochytrium* sp. have been published in the literature. For this reason, it was decided to carry out a review regarding the polysaccharides with the monomeric unit of L-galactose and the *Rhodophyceae* family.

Polysaccharides of a structural type of galactose are widespread throughout the *Rhodophyceae* (Rees 1965, Anderson and Rees 1966). Superficially different polysaccharide preparations such as agars, carrageenans, porphyrans, among others, are included in this group. All of these are defined as galactans which are polymers of galactose, and which were first detected in 1892 (Schulze and Steiger, 1892). They have a large number of applications including stabilizing, viscosifying, gelling, and emulsifying agents, but only agar and carrageenans have been agreed upon as food additives. These galactans are sulphated and have no equivalent in terrestrial plants and can constitute up to 70% of the dry matter of some red algae. In this perspective, during these last two decades many research efforts were made to optimize the conditions for its large-scale production, for structural research and for the characterization of its rheological and biological properties. Next, it is shown how the polysaccharides called galactans are cataloged and their differences regarding their chemical uniqueness, their solubility, and their molecular weight.

1.2.3 Galactans

Over the last few decades, many biological and rheological properties of polysaccharides and oligosaccharides have been described. Galactans, and more especially sulfated galactans from seaweed, have shown interesting and specific properties not only as texturizing agents, but also as biological active compounds in various organisms.

Figure 1.1 shows the classification of galactans described by Delattre et al. [19]. This classification of polysaccharides includes classic sulfated galactans extracted from seaweed, and classified as agar and carrageenans. However, some galactans are more complex, and their specific structural characteristics have been

characterized after their extraction not only from terrestrial plants and marine algae, but also from animals and microorganisms.

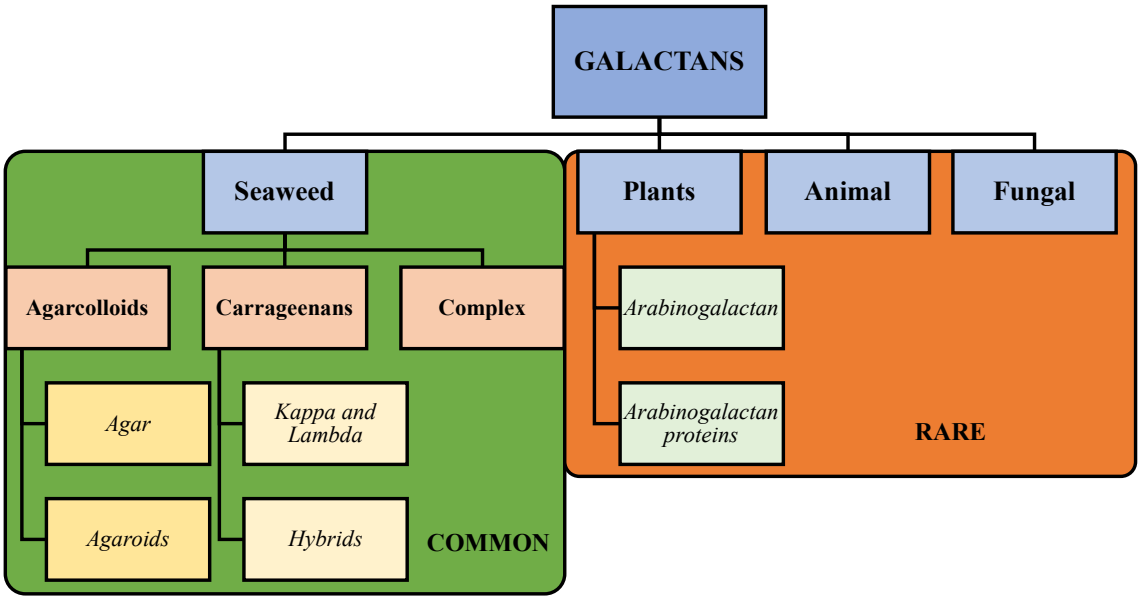

Figure 1.1. Classification of galactans.

Previous works in the study of the microalgae *Schizochytrium* sp. do not show specific results regarding its molecular chemical structure, solubility and molecular weight. Such a bibliographic review was carried out that encompasses the classification described by Delattre et al. [19] and the previously mentioned aspects in order to classify the microalgae *Schizochytrium* sp. and have a clearer vision of the reaction mechanism that is proposed for this investigation. Table 1.1 shows the proposed classification of galactans, their chemical characteristics, solubility and molecular weight.

1.3 Synthetic polymers

Synthetic polymers are macromolecules formed by the union of monomers, obtained in an artificial way. These polymers make it possible to manufacture synthetic fibers with the aim of developing functional products such as textiles and medical devices. In the synthesis of polyamide, a detailed quality control is carried out in order to regulate the thickness and uniformity of the fibers for use in various

applications. Examples of this type of compound are polyethylene, Nylon and Bakelite.

Properties of some synthetic polymers are shown in Table 1.2.

Previous studies of synthesis and characterization of poly (acrylic acid-co-itaconic acid) hydrogels for removal of metal oxides on surfaces involved an addition polymerization process using the N-N'-methylenebisacrylamide agent as a precursor. This additive, widely used in the synthesis of hydrogels, is toxic, which led to several current studies investigating new hydrogels based on natural crosslinkers, naturally crosslinked polymers, or the use of synthetic derivatives in natural polymers such as chitosan.

1.4 Natural hydrogels

Physically cross-linked hydrogels using polysaccharides such as alginates or xyloglucans have numerous advantages over chemically cross-linked ones [26]. Chemically cross-linked hydrogels need long periods of degradation; in addition, the trapped substances can be damaged, causing a loss in their activity. For this reason, various copolymers are currently being studied using polysaccharides, proteins, among others for the controlled release of drugs [27].

Examples of this are hydrogels that use genipin, a natural crosslinker that reacts with amino groups to form closed mesh networks that give it the ability to retain solutions inside. Figure 1.2 visually shows the crossover that occurs with genipin.

Another polymer with good biodegradatability, biocompatibility and good mechanical resistance capabilities is chitosan. Chitosan is a naturally-based polymer, obtained by alkaline deacetylation of chitin, which has excellent biological properties such as biodegradability, immunological, antibacterial, and healing activity. Recently, there has been a growing interest in the chemical modification of chitosan in order to improve its solubility and expand its applications. The main chemical modifications of chitosan can be seen in Figure 1.3. These chemical modifications led to a many derivatives with a wide range of applications.

Among the many macromolecules that can be used for hydrogel formation, polysaccharides are extremely advantageous compared to synthetic polymers that are widely present in living organisms, and are often produced by recombinant DNA techniques. These natural hydrogels come from renewable sources, giving them an economic advantage over synthetic polymers. Polysaccharides are generally non-toxic, biocompatible, and exhibit a number of unique physicochemical properties that make them suitable for different applications in drug delivery systems. Some polysaccharides that have been studied and exploited in several fields related to pharmacology are shown in Figure 1.4.

Table 1.1. Classification of galactans regarding their chemical uniqueness, solubility, and molecular weight.

Galactans		**Chemical structure**	**Solubility**	**Mw**
Agar	Agarose	3,6-α-L-anhydrogalactopyranose, 2% sulfated, high methylated (<20%)	Non-soluble at room temperature	120 kDa
	Agaropectin	As agarose but with sulpahtes, pyruvate, glycuronate, methyl	Non-soluble	400 kDa [20]
Agaroids		As agarose but replace 3,6-anhydrogalactose for 4-α-L-galactopyranose, 20% sulfated, e. g. funorans and porphyrians	Soluble [21]	110 kDa [22]
Carrageenans Kappa y Lambda		3,6-α-D-anhydrogalactopyranose, high content of esther-sufate groups (20-40%)	Soluble [21]	18-200 kDa [23] 1742-3123 kDa [24]
Hybrid Carrageenans		Two different carrageenans	Soluble [21]	1132 kDa [24]
Complex		Same sequence branched by hexoses and / or pentoses (galactose, glucose, xylose, etc.)	Soluble [25]	60 kDa [25]

Table 1.2. Synthetic polymers properties

Polymer	Features
Polyamide	Highly resistant to fracture and elastic. They have the advantage that they do not decompose, although they tend to deform with heat.
Acrylate	Photoresistivity
Polyester	They are one of the most economical synthetic polymers and widely used to make clothing and sportswear.
Polyvinyl	They have resistance to chemical products and agents.
Polyethylene	Friction resistance
Polypropylene	Support all kinds of treatments, remaining unchanged.
Elastomer	High elasticity polymers

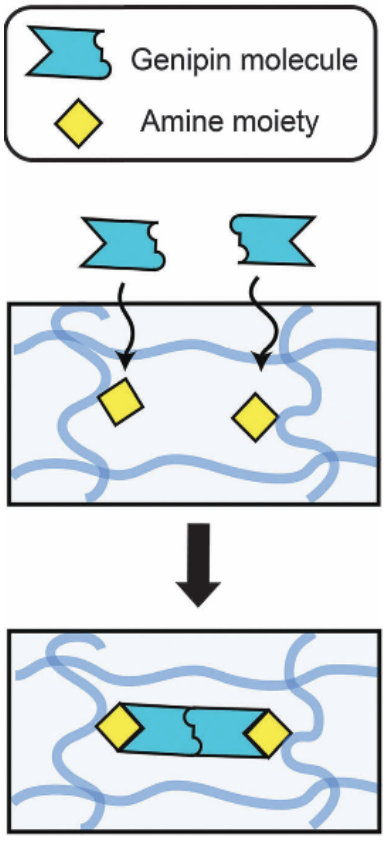

Figure 1.2. Cross-linking using genipin. Ninh, et.al (2015).

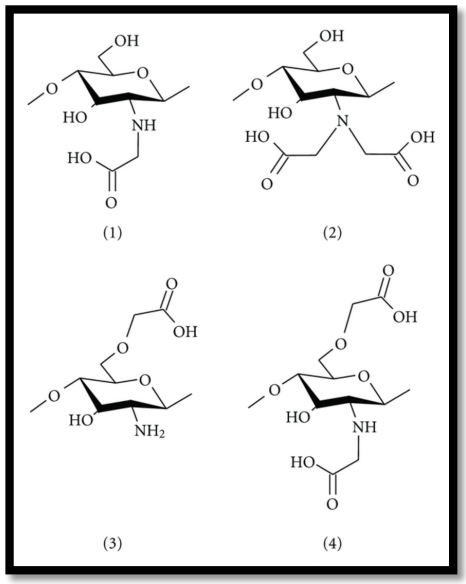

Figure 1.3 Chitosan derivative: N, O-carboxymethyl chitosan.

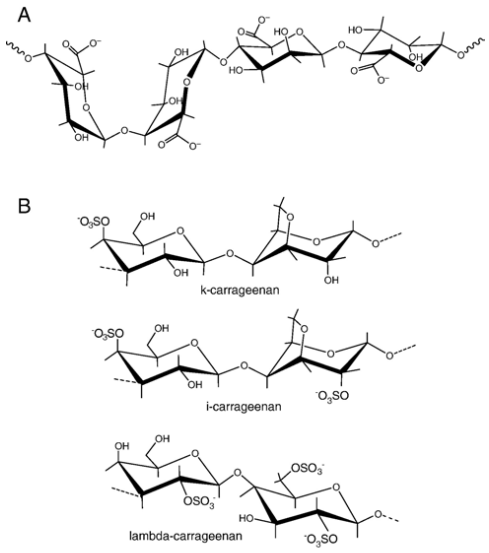

Figure 1.4 Polysaccharides for the production of natural hydrogels: (A) Alginate, (B) Carrogens.

1.5 Semi-synthetic polymers

Due to its chemistry, various studies indicate that the polymerization of synthetic polymers with polysaccharides for the development of composites is possible, and its current application is found in the treatment of wastewater and

superabsorbents [17,28,29]. For example, in 2014 Chauhan et al. [16] synthesized microalgae-acrylic acid and microalgae-acrylamide composites where the microalgae were extracted directly from a fresh water source (without reporting their species), and under a cell wall separation procedure [23–27] they were polymerized with the monomers. These copolymers were subjected to a residual water treatment in order to obtain a reduction of silicates in pipes and thus avoiding frequent maintenance in industrial equipment.

The research in this thesis proposes a route of polymerization of acrylic acid with a microalga. Thus, the microalgae *Schizochytrium* sp. could react with acrylic acid monomers to form an innovative polymer with new properties and possible biomedical and/or environmental applications.

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CHAPTER 2. HYPOTHESIS AND OBJECTIVES

2.1 Hypothesis

The hydroxyl groups (–OH) of the polysaccharides of *Schizochytrium* sp. and the double bonds of the acrylic acid monomer will promote a polymerization reaction that will form a hybrid polymer with new physicochemical, thermal and mechanical characteristics. In addition, changes in the purification process and concentration of *Schizochytrium* sp. could modify the physicochemical, mechanical and thermal properties of the new polymer.

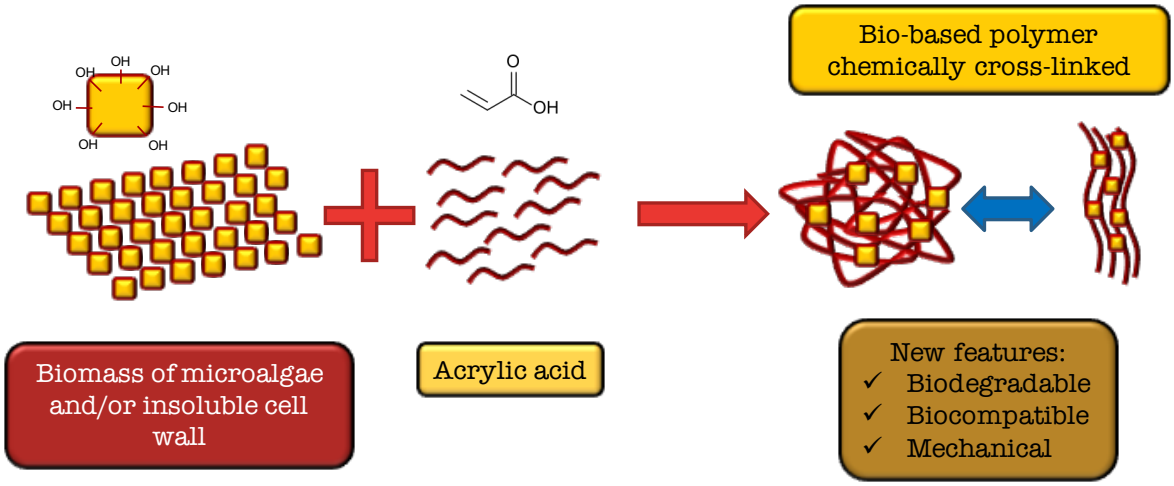

Figure 2. Proposed synthesis of acrylic acid–*Schizochytrium* sp. bio-based polymer.

2.2 General objective

Synthesize an innovative biopolymer based on acrylic acid/*Schizochytrium* sp. using microalgae biomass (SCZ) and its insoluble wall fractions (FIP). Determine the effect of the synthesis parameters on the thermal, physicochemical and mechanical properties of the material.

2.3 Specific objectives

- Develop a pickling method based on poly (acrylic acid) (PAA) for its use in the removal of Fe and Cu oxides from metallic surfaces.
- Cultivate microalgae and make isolation of insoluble fraction of cell wall *Schizochytrium* sp. (FIP).
- Perform the synthesis of PAA-SCZ and PAA-FIP copolymers.
- Determine the chemical composition, mechanical properties and thermal stability of copolymers.
- Determine the kinetics of swelling at physiological pH of 1.2, 7.4 and 9 of the PAA-SCZ hydrogels to observe their viability as vehicles for drug transport.
- Synthesize and characterize PAA–FIP at different concentrations of FIP and compare them with PAA–SCZ to determine the effect of biomass on copolymers.
- Evaluate the hydro-degradation of PAA-FIP copolymers.
- Corroborate the presence of polysaccharides and proteins in the FIP by TGA and Lowry analysis respectively.
- Characterize the morphology of the *Schizochytrium* sp. (SCZ), the insoluble wall fraction (FIP) and the hybrid biopolymers (PAA-SCZ and PAA-FIP).
- Determine the thermal stability of the SCZ and the hybrid biopolymer (PAA-SCZ).
- Identify the functional groups of the SCZ, FIP and the extract to evaluate the reaction mechanism.
- Evaluate the mechanical properties of PAA-SCZ.

TUNING THE PH-RESPONSIVENESS CAPABILITY OF POLY(ACRYLIC ACID-CO-ITACONIC ACID)/NAOH HYDROGEL: DESIGN, SWELLING, AND RUST REMOVAL EVALUATION

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A NOVEL ACRYLIC ACID-*SCHIZOCHYTRIUM* SP. BIO-BASED POLYMER: DESIGN, SYNTHESIS, AND PROPERTIES

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CHAPTER 5. GENERAL CONCLUSIONS

It was demonstrated that PAA-co-IA hydrogel is a suitable material for the elimination of rust grown on metallic surfaces. It was proven that copolymer formation and neutralization of carboxylic acid groups during the polymerization reaction highly improved the hydrogel removal capabilities as well as its swelling ability. The highest hydrogel swelling was found at pH:ASS 11, in contrast, the highest metal rust removal was observed at pH:ASS 4; demonstrating that pH plays a significant role in both processes. Remarkably, the capability of PAA-co-IA hydrogel for Fe rust removal was almost four times greater than similar studies. It was identified that the removal mechanism was first governed by the surface adhesiveness of hydrogel on metallic plates followed by diffusion and metal oxides phase dissolution, which was favored by the acidic medium that filled the hydrogel network. This combined mechanism involved intermolecular forces as well as the formation of metal-coordinated species into the polymeric matrix. This innovative process presented the advantage of being environmentally friendly, and is user-friendly; and in case of interest, the metallic phases can be recovered by simple polymer carbonization.

Novel bio-based polymers of PAA-SCZ and PAA-FIP were synthesized for the first time. Morphological and physicochemical characterization of *Schizochytrium* sp. (SCZ) and its insoluble cell-wall fraction (FIP) proved the conformation differences between the two kinds of biomass. Subsequentially, it was corroborated that water-soluble carbohydrates and proteins were removed during the cell fracture procedure. The physicochemical and thermal characterization (IR, NMR, TGA, and DSC) of PAA-SCZ and PAA-FIP biocomposites confirmed both physical and chemical crosslinking. Moreover, it was demonstrated that composites' properties (thermal, elasticity, and hydrolytic stability) could be tunable using SCZ or FIP upon changing their respective concentration. The SCZ and FIP concentrations also induced a significant change in the glass transition temperature (T_g). From the mechanical analysis, it can be concluded that PAA-FIP (30%) has the highest elongation yield (715%), which is understandable as more functional

groups are available to form chemical and intermolecular bonds. Furthermore, the hydrolytic studies presented a higher super absorbance degree (~30000%) than other PAA hydrogels reported in the literature. However, the decrement in the swelling properties indicates the fragility of the physical-crosslinking. These findings reveal a new polymeric material that can be introduced as an alternative to reduce the use of fossil reserves while providing tunable properties. Nonetheless, more studies are necessary to know their real potential application on an industrial scale.

APPENDIX. PAPERS AND CONGRESSES

Papers

Papers related to thesis

1. Olvera-Sosa, M., Guerra-Contreras, A., Gómez-Durán, C. F., González-García, R., & Palestino, G. (2020). Tuning the pH-responsiveness capability of poly (acrylic acid-co-itaconic acid)/NaOH hydrogel: Design, swelling, and rust removal evaluation. *J. Appl. Polym. Sci.*, **137**(8), 48403. (Published).
2. Olvera-Sosa, M., Rosales-Mendoza, S., García-Briones, G. S., Betancourt-Mendiola, M. D. L., González-Ortega, O., & Palestino, G. (2021). A novel acrylic acid-Schizochytrium sp. bio-based polymer: Design, synthesis, and properties. *Mater. Today Commun.*, **102029**. (Published).

Papers on collaboration

1. García-Briones, G. S., Olvera-Sosa, M., & Palestino, G. (2019). Novel Supported Nanostructured Sensors for Chemical Warfare Agents (CWAs) Detection. In *NATO Advanced Research Workshop on Nanoscale Materials for Warfare Agent Detection* (pp. 225-251). Springer, Dordrecht. (Published).
2. Chazaro-Ruiz, L. F., Olvera-Sosa, M., Vidal, G., Rangel-Mendez, J. R., Palestino, G., Perez, F., & Zhang, W. (2020). Synthesis of Bamboo-like Multiwall Carbon Nanotube–Poly (Acrylic Acid-co-Itaconic Acid)/NaOH Composite Hydrogel and its Potential Application for Electrochemical Detection of Cadmium (II). *Biosensors*, **10**(10), 147. (Published)
3. Guerra-Contreras A., Camacho-Ramírez A., Olvera-Sosa M., González-García R., & Palestino, G. (2021). Evaluation of a rapid and long-effective pickling method for iron rust removal on metallic surfaces using carboxylic acid-based polymers. *J. Polym. Res.* (Summited).

4. García-Silva, I., Olvera-Sosa, M., Ortega-Berlanga, B., Ruíz-Rodríguez, V., Palestino, G., Rosales-Mendoza, S. (2021). Synthesis and characterization of innovative nanogels based on polyacrylic acid and microalgae cell wall and their potential as antigen delivery vehicles. (Peer-review).

Symposiums and Congresses

1. 1st International Symposium on Functional Porous Materials (2016).
2. XXXVII Encuentro Nacional de la AMIDIQ (2016).
3. Programa de Inducción a la Innovación y al Emprendimiento y Concurso de Exhibición de Carteles de Proyectos de Investigación (2016).
4. Entre pares. Publicar y navegar en redes de información científica. 5º Aniversario (2016).
5. XXVI International Materials Research Congress (2017).
6. Primer Encuentro de Ingeniería Química. XXV Aniversario del Posgrado en Ciencias en Ingeniería Química (2017). **Awarded with the First Place**.
7. 4to. Simposio Potosino de Investigación en Ciencia de Materiales (2018).
8. Segundo Simposio de Temas Selectos de Química (2018).
9. XXVII International Materials Research Congress (2018).
10. XXVIII International Materials Research Congress (2019).
11. Segundo Encuentro de Ingeniería Química (2019).
12. Nanotecnología y sus aplicaciones en el área de la Química (2020).

Training Courses

1. 8th International Training Course. Course from In Situ to Operando Studies (2018).
2. Segundo Curso-Taller: Eliminación de Compuestos Tóxicos del Agua: Caracterización de materiales y aplicaciones (2019).