UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ

Doctorado Institucional en Ingeniería y Ciencia de Materiales

Application of Mechanochemical Procedure on Aqueous Cr(VI) Removal with Additives of Activated Carbon and Fe^0/Fe_2O_3

TESIS

QUE PARA OBTENER EL GRADO DE

DOCTOR EN INGENIERÍA Y CIENCIA DE MATERIALES

PRESENTA

Yi Fang

ASESOR

Dr. Alejandro López Valdivieso

Dr. Changsheng Peng

PATROCINADO POR CONACyT Beca número 900339

San Luis Potosí , S.L.P. Marzo 2022

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Abstract

The green technique of mechanical ball milling has been extensively employed in the fabrication of environmentally functional materials. The improved specific surface area and modified surface properties of the resulting materials contribute to the high performance in pollutant removal. In this work, to improve the performance of low-cost activated carbon and sponge iron powder under neutral conditions. Ball milling was used to pretreat activated carbon and treat the mixture of surface oxidized sponge iron powder and contaminant solution, wherein the strong oxidant and toxic Cr(VI) was chosen as the target pollutant. The reduction coupling with precipitation was dominantly attributed to the removal of Cr(VI), wherein the surface enhanced surface functional groups and hydrophilicity within ball milling were the main mechanisms subject to the elimination of Cr(VI) which was substantiated by Boehm's titration. Furthermore, surface precipitated Cr(III) oxides have been shown to impede Cr(VI) removal, and acidic washing experiments can rejuvenate the used activated carbon by dissolving the Cr(III) oxide layer. Moreover, the reduced Cr (III) and adsorbed Cr (VI) can be recovered by acidic and alkaline elution, respectively.

The inherent demerits of zerovalent iron, such as surface passivation in solution and low electron efficiency, could be mitigated perpetually by ball milling. Removal efficiency of Cr(VI) maintained over 60 % over a wide pH of 4-10 in presence of ball milling, while negligible Cr(VI) decrease was noticed in absence of ball milling. XPS spectra analysis supported that reduction of Cr(VI) to Cr(III) followed co-complexed with Fe(III) as $Fe_{0.33}Cr_{0.67}(OH)_3$(s) was the foremost elimination pathway of Cr(VI). The effect of dissolved oxygen on Cr(VI) removal can be divided into two segments as per the pH; the generated Fe(II) that originated from the Fe^0 oxidation by dissolved oxygen facilitated to the reduction of Cr(VI) at acidic conditions, whereas the produced Fe(II) ions were oxidized at alkaline conditions and the electron efficiency of Fe was alleviated likewise. Uncovered fresh core Fe^0 to the aqueous Cr(VI) by the motion of ball milling which was the main mechanism that diminished the surface passivation layer of Cr(III)/Fe(III) hydro(oxides). Furthermore, the depletion curve of Cr(VI) as function of time under different initial concentration, dosage, and rotational speed was

consistent with zero order kinetic model.

Keywords: Mechanochemical Procedure, Ball Milling, Activated Carbon, Zero-Valent Iron, Chromium, Reduction

CONTENT

Index of Figures

Index of Tables

Chapter I. **Introduction**

Mechanochemical procedures (MCPs) as an emerging technology for nanomaterial (nano-zero valent iron, nano activated carbon) preparation, has arouse more and more attentions by researchers[10-15]. MCPs is fast become a key technology in environmental material synthesis with sustainable and low-cost. And physical and chemical characteristics of materials will be enhanced like hydrophilic and adsorption performance on inorganic matters[16, 17]. In general, MCPs defect the material particle through shear and impact force generated from high energy collision between milling balls and medium. The size of medium particles or grain declined rapidly after undergoing repeat flatten, deformation, disintegration, and the size of medium won't further refined even longer milling duration executed due to the cold-welding and agglomeration of particles[19]. In addition to the particle size reduction, when mixed desired medium with functional agents like active metal and organic matters to produced specific characteristic materials. The evidence of target material modification assistant with mechanically milling can be clearly seen in the case of study of Yulin Zheng et al, in which the MgO introduced into milling jar with biochar to prepare dual-functional adsorbent for cationic dye and anionic phosphate removal, the adsorption performance of MgO-biochar improved significantly compared to the pristine biochar[25]. Common equipment for MCPs are planetary ball-milling, tumbler ball-milling, attrition ball-milling and vibration ball-milling, details seen in Fig 1-1, when considering the size limitation for laboratory-scale application; the planetary ball-milling of high rotate speed, compact size and multiple milling jars was an optimum choice for laboratory trial.

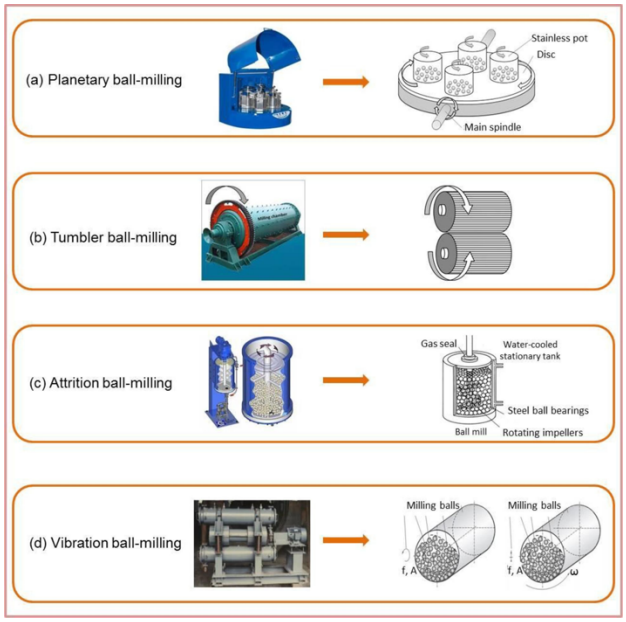

Figure. 1-1 Four conventional ball-milling machines and their working principles[26], (a) planetary ball-milling, (b) tumbler ball-milling, (c) attrition ball-milling, (d) vibration ball-milling, copyright 2020, Elsevier.

Chromium is widely used in industry as plating, alloying, textile dyes and pigments. Due to the wide application of chromium in industry, the consequent environment contamination has become a central issue and has arouse the attention of researchers [27-30]. Cr (VI) exists in the forms of chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and CrO_3 are considered to be the most toxic forms of chromium, chromium poisons the plants in the form of hexavalent chromium for its highly mobile and toxic while trivalent chromium is less mobile and toxic (Deepti S et al., 2018). Cr(III) is an essential micronutrient to human, while Cr(VI) is toxic and can cause severe diseases such as kidney circulation, dermatitis and lung cancer[29]. Therefore, attention should be activated for sequestration or reduction Cr(VI) to Cr(III) from aquatic environments for the protection of environment and public health.

The conventional methods for the removal of Cr(VI) from wastewater are membrane filtration, precipitation, and ion exchange[28]. There are some disadvantages of these methods including high chemical dosage, high capital and operation cost, high energy consumption and potential secondary effluent[27]. The activated carbon (AC) is

the most widely used material for its readily available, low cost, high specific surface area which range from 500 to 1500m^2 g^{-1}, developed internal microporous structure and wide spectrum of surface functional groups like carboxylic group[31]. AC derived from biomass like coconut shell, wood coal, hazelnut shell, *Terminalia arjuna* nuts and rubber wood sawdust, the adsorption capacity of synthetic adsorbent from these biomass on Cr(VI) range from 4.4 to 170.0 mg g^{-1} [32-35]. In order to further improve the adsorption performance of AC, modification of the activated carbon by chemical procedure to enhance its surface functional group, AC was prepared from *Longan* seed by chemical modification with sodium hydroxide (NaOH) which possess adsorption capacity on Cr(VI) was 35.02 mg/g and higher than the pristine AC[36]. AC pretreated by heating with sulfuric acid and nitric acid, the maximum adsorption capacity are 7.485 and 10.929 mg/g, respectively[37]. By way of illustration, Kronje,K,J et al activated the sugarcane bagasse by zinc chloride, results indicated that the removal rate was over 87%[38]. Compared to the chemical modification, physical treatment presents several advantages, no secondary effluent after physical treatment and easily operation. Conventional physical treatment are activation with steam, gasification in CO_2 or in a water-nitrogen mixture[39, 40].

Most of the adsorption treatments were pre-adjusted to the acid condition and the pH value were 2-4[29, 41-43]. At the acid condition the surface function group were protonated and facilitated the redox reaction between contaminants and electron on AC. But the adjustment of acid condition required numerous acid solution and subsequently cause the emission problem of acidic effluent. Augment the removal capability of AC at near-neutral pH could be a promising solution for removal of Cr(VI).

On the other hand, improving the adsorption capacity of activated carbon through mechanical grinding rarely seen in the related research literatures[44-49]. Crushing the activated carbon particle into finer particle by ball milling, the activated carbon become smaller particulate in the process of milling, thus more surface functional groups were exposed and higher specific surface area, the adsorption performance could be

improved, correspondingly.

Zero-valent iron as another common low-cost material has received much attention on contaminants removal, while the inherent demerits of zero-valent iron like easily-agglomeration, atmospheric oxidation, passivation in solution and the low electron efficiency have inhibited its implication. MCP could remove the surface oxidation layer through the repetitive collision which makes it a promising method on mitigating the drawbacks and improving the lifespan of zero-valent iron.

1.1. The sequestration of aqueous Cr(VI) by zerovalent iron-based materials

1.1.1. Introduction

Chromium (Cr) has a wide range of industrial applications such as plating, alloying, leather tanning, metallurgy, textile dyes, and pigments. Thus, Cr-contaminated sewage has become a big issue and has attracted the attention of experts to eliminate Cr by employing various kinds of materials like activated carbon [27], alkalic modified activated carbon [29], green synthesized zero-valent iron [28, 50, 51] and well-designed nanocarbon spheres [30]. Cr mainly occurs in two different states in nature such as hexavalent chromium (Cr(VI)) and trivalent chromium (Cr(III)). Cr(VI) has mutagenic and carcinogenic effects in humans because of their higher mobility and toxicity behavior. It can cause severe diseases such as kidney circulation, dermatitis, and lung cancer in humans [29]. While, Cr(III) is less mobile, more stable, and less toxic than Cr(VI) [52]. It can be converted into chromium hydroxide ($Cr(OH)_3$), which can be precipitated out at moderately acidic to alkaline pH and can also serve as an essential micronutrient. Therefore, the removal or reduction of Cr(VI) anions to nontoxic and immobile Cr(III) ions is important for protecting the environment and public health.

Moreover, conventional methods such as adsorption, reduction, membrane filtration, precipitation, and ion exchange have been employed to remove heavy metals from sewage [28, 53]. Whereas, the reduction and adsorption procedure of Cr(VI) has

attracted more attention because of its cost-effectiveness as compared to membrane filtration [54], ion exchange [55], and electrochemical treatment technologies [35]. Further, iron and modified iron compounds have been extensively applied for Cr(VI) elimination owing to having their higher activity and feasible synthesis protocols such as green technologies [28, 50, 51, 56], mangrove fungus reduction method [57], in-situ growth method [58] and replacement reactions method [59]. Further, the nanoparticles of ZVI have shown a great potential application in the treatment of real tannery wastewater and the removal ratio of 100, 70, 73, and 88% were noticed for Cr(VI), TOC, COD, and phenol, respectively [60]. Since the first exhaustively documented practical application of ZVI on groundwater remediation with the permeable reactive barrier (PRB) in 1996 [61], the development of ZVI-based materials has received considerable attention for environmental remediation. Regarding this, Fig. 1-2 is depicting a comprehensive summary of the advancements in ZVI-based materials for sewage treatment.

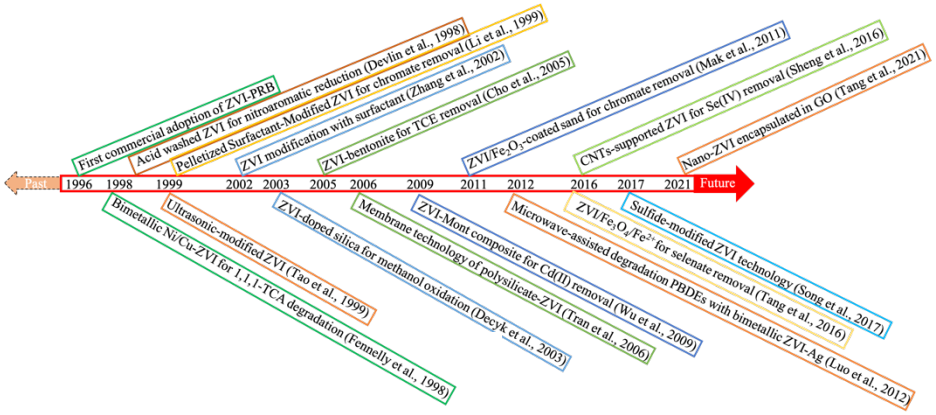

Figure. 1-2 The major events of ZVI-based materials development over the past 25 years (1,1,1 TCA (1,1,1-trichloroethane), TCE (trichloroethylene), Mont (Montmorillonite), CNTs (carbon nanotubes), PBDEs (polybrominated diphenyl ethers), GO (graphite oxide)) [1, 2 3 4 5 6 7, 62 8 9 18 20, 63 21, 22]

Notably, certain factors such as particle size [64], pH value [65, 66], co-existing ions [67, 68], hydrodynamic filed [69] and contaminant concentration were restricted performance of iron [70]. The passivation layer on the surface of the iron particle formed under alkaline conditions could sequester the electron derived from iron, wherein the passivation layer

was mainly contained non-conductive hydroxide of iron and Cr [71]. Research efforts have been done on impairing the effect of the passivation layer. For instance, the iron/aluminum bimetallic material presented higher Cr-elimination performance as compared to the elemental iron [72]. In addition to unfavorable impacts induced by the surface oxidized layer, nZVI particles are preferred to clump in the aqueous solution where the activities of iron were limited remarkably [73]. To solve this issue, a stable nZVI containing material was synthesized through embodied nZVI in MCM-41 for the improvement of the performance and longevity of nZVI in solution [74]. The most common measures to promote the capability of iron include composited bimetallic materials (Al-Fe, Zn-Fe, Pb-Fe, Cu-Fe, Ni-Fe, Ag-Fe) [75, 76], loaded iron on carbon template [77], and mixed iron with elemental sulfur or sulfide [78]. The preparation procedures for iron-bearing materials fluctuate by considering the limitations caused by poor solution dispersion and easy air oxidation of iron. To enhance the dispersion of nZVI in solution, carbon nanotube-supported nZVI was synthesized through liquid-phase reduction method and Cr removal efficiency was found to be around 36% higher than bare nZVI [79]. While, the reduction of 10 ppm Cr(VI) solution to ~1ppm was observed in three days by employing activated carbon-supported iron prepared by carbothermal reduction technique [77]. Similarly, the carbon skeleton improved the stability of iron dramatically [80].

Therefore, a comprehensive summary of ZVI-based materials development was essential to design a compatible environmental material with practical contamination sites. Even though some review papers have recapitulated the versatile ZVI technology from the synthesis procedure to different countermeasures against the limitations of pristine ZVI [81, 82]. As well as another review paper has discussed the effect of solution chemistry and operational conditions on ZVI property [83]. Rare review papers systematically considered the co-effect of pH and DO on the performance of ZVI-based materials on targeted pollutant sequestration. For example, the efficiency of ZVI towards Cr(VI) removal was suppressed in the presence of oxygen [84], but another study

discovered the opposing results in the presence of oxygen [85]. Briefly, the pH could greatly involve in the corrosion of ZVI and product establishment with DO. Therefore, we delicately evaluated the co-effect of pH (acid or alkaline) and DO (oxic or anoxic) on the capability of ZVI-based materials. Moreover, the literature involved in the preparation methods of ZVI-based materials (liquid-phase reduction and mechanical methods), four common ZVI-based materials (carbon-ZVI, sulfur-ZVI, bimetal of ZVI, and magnetite-ZVI composites), mechanism of Cr(VI) elimination, field application, and market penetration of ZVI-based materials were carefully discussed herein.

1.1.2. Synthesis of ZVI-based Materials for the Removal of Chromium

Various technologies can be classified into chemical and physical methods for the fabrication of ZVI-based materials to remove Cr from the environment. Chemical reductants (such as molecular hydrogen, hydrazine hydrate, $NaBH_4$, CO, etc.) were applied for Cr-reduction. While, the physical methods comprised mechanical crushing and metal electrode precipitation [86]. To the best of our knowledge, most of the researches only focused on the application of chemical reduction methods by using $NaBH_4$ [87] and mechanical milling [88, 89].

1.1.2.1 Liquid-phase Reduction

The liquid-phase reduction or borohydride reduction method is based on ferric and ferrous ions as ZVI precursors and $NaBH_4$ as a reducing agent. The earliest recorded prepared nano-scale ZVI was $FeBr_2$(aq) and $FeBr_3$(aq), which were reduced by $NaBH_4$ in the aqueous solution [90]. Similarly, various other researchers synthesized nano-scale ZVI with narrow size distribution (10-100 nm) [91, 92] and also coated with oxide shells [93]. For its preparation, the desired amount of Fe precursor such as degassed $FeCl_3$ solution was dropped with sodium borohydride solution (1 drop/s), the reduction reaction is presented in Eq (1-1). After the accomplishment of the reaction, the mixed solution was allowed to settle down for 20 min, and then it was centrifuged for

collection of ZVI [94]. The synthesis process was conducted under an inert atmosphere as-synthesized ZVI can be easily oxidized in air.

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2\,(gas) \quad (1\text{-}1)$$

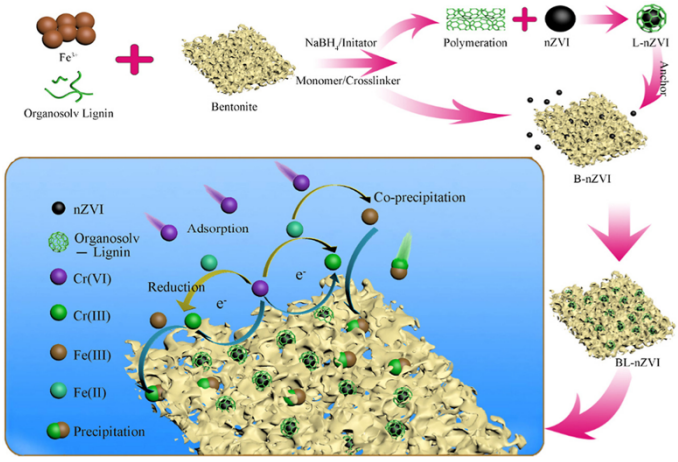

Figure. 1-3 The schematic illustration of the preparation of BL-nZVI by liquid-phase reduction method, and the removal process of Cr(VI). The Cr(VI) was reduced by loaded-ZVI and followed co-precipitation with Fe(III) [95], Copyright 2020, Elsevier.

Although extensive research has been carried out on bare ZVI preparation, the reactivity of nZVI might be lowered due to agglomerate irreversibly in the solution. ZVI doped on the template such as activated carbon [96], biochar [97], graphite [98] and chitosan [99] has demonstrated outstanding dispersion in the solution. Meanwhile, the removal performance of Cr(VI) was improved considerably for ZVI-loaded material concerning their monometallic counterpart. A group of researchers successfully produced biochar-supported nZVI by liquid reduction technique, wherein nZVI was loaded on biochar through carboxyl and silicon mineral within biochar. The removal capacity for Cr(VI) was 40 mg/g under initial pH 4.0 and could serve as a candidate material for groundwater remediation [100]. Further, as compared to non-supported nZVI (62.9%), the attapulgite-supported nZVI exhibited 90.6% removal efficiency for Cr(VI). Moreover, the stability and dispersion of nZVI were improved after doping evenly on a supporter of attapulgite [101]. A team of researchers performed a series of experiments

to illustrate that bentonite-supported organosolv lignin stabilized nZVI (BL-nZVI) had a higher removal capacity of Cr(VI) than bare nZVI and bentonite-supported nZVI (B-nZVI) [95]. A comprehensive procedure from synthesis to the application has been demonstrated in Fig. 1-3.

1.1.2.2 Mechanical Method

The ball milling (BM) procedure has been proved to be an effective method for the preparation of nZVI [102]. Briefly, the iron grains undergo deformation, fracture, and welding repeatedly in the presence of vigorous collision between milling medium balls and iron particles. The size of the produced ZVI is a function of grinding duration time [103]. Further, the ZVI fabricated by mechanical milling subjects to the coarse size and unregulated shape, but the BM method can easily be scaled up with reasonable expenditures as compared to other approaches [104]. It was reported that the 2 mm grain of ZVI was milled in high energy planetary ball milling for 10 h, and the resulting 20.9 μm meso-ZVI eradicated Cr(VI) and organic pollutant effectively [105]. Recently, it was reported that different masses of AC were combined with 5.6 g of micron-scale ZVI (mZVI) in stainless steel milling jar and then grounded for 30 minutes at 300 rpm. Thereafter, it was followed by the addition of mZVI-AC in acidic and anaerobic Cr(VI) solution. The removal efficiency of Cr(VI) reached 94.01% within 2 h, it was also found that only 22.1% Cr(VI) was removed by the mixture of ZVI and AC [106]. These results verified the findings of a great deal of the previous work of Wang et al, (2020), and their thorough information has been presented in Fig. 1-4 [107].

Besides, the milling-induced displacement reaction to prepare various sizes of ZVI is a promising technology, as it could enable the recycling of scrap iron. The nanocomposites of ZVI with Al_2O_3 or ZnO were obtained after grinding of a sample of metallic aluminum or zinc with magnetite or hematite [108-110]. As the reaction processes have been presented in Eqs (1-2)-(1-4). Thus, by considering the ease of operation, cost-effectiveness, and readily scaling-up, BM is a promising technology for ZVI

preparation.

$$3Fe_3O_4 + 8Al = 3Fe + 4Al_2O_3 \quad (1\text{-}2)$$

$$Fe_3O_4 + 4Zn = 3Fe + 4ZnO \quad (1\text{-}3)$$

$$Fe_2O_3 + 2Al = 2Fe + Al_2O_3 \quad (1\text{-}4)$$

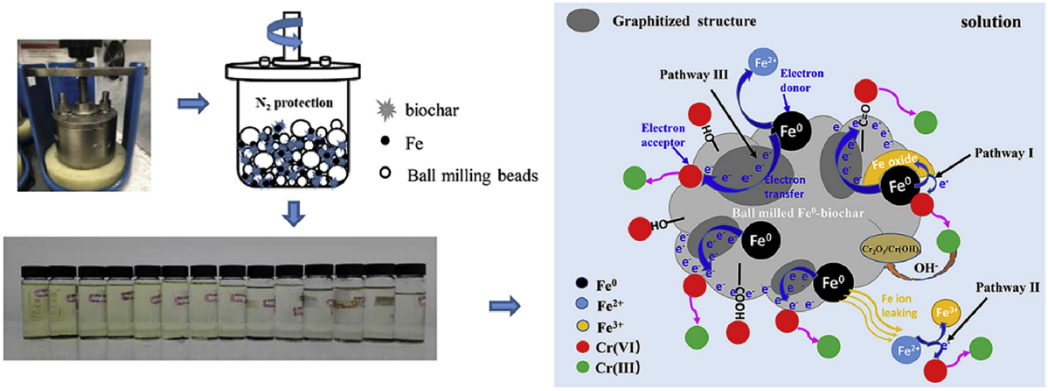

Figure. 1-4 The schematic illustration of the preparation of the biochar-supported ZVI by mechanical ball milling and its application for the Cr(VI) removal. The adsorbed Cr(VI) on pore channel and surface functional groups of biochar was reduced by Fe^0, meanwhile, part of Cr(VI) reduced in solution (Wang et al., 2020c), Copyright 2020, Elsevier.

1.1.2.3. Other synthetic methods

Apart from the numerous studies about chemical reduction and mechanical milling, there are also other non-widely discussed approaches for ZVI fabrication. For instance, the coal and iron oxide (FeO, Fe_2O_3, Fe_3O_4) were introduced into a silica glass tube equipped with a graphite cylinder radiation heater, the coal reacted with H_2O and CO_2 to produce reductant gas CO and H_2 over 800℃, and then CO and H_2 reduced iron oxides to ZVI via the thermal reduction method [111]. Similarly, the goethite was reduced to ZVI by H_2 with heat, nevertheless, the reducing reactant not only included ZVI but also magnetite [91]. Further, the chemical vapor condensation (CVC) process could decompose iron pentacarbonyl ($Fe(CO)_5$) under Ar or He atmosphere to prepare nZVI. Thus, the spherical nZVI (6-25 nm in diameter) was successfully prepared by CVC at

150℃ [112]. Moreover, pulsed electrodeposition (PED) was adopted to reduce aqueous iron salt to ZVI by desired current and voltage. In short, sacrificial iron anode and inert Ti cathode were immersed in $(NH_4)_2Fe(SO_4)_2$-contained electrolyte and were pulsed continuously. Thus, Fe^{2+} ions were reduced to Fe^0 and precipitated on Ti cathode [113]. A similar study was performed with PED to obtain nZVI with an average diameter of 19 nm [114]. The previously described spinning disk reactor (SDR) method proposed potential application on nZVI synthesis on the laboratory-scale [115]. Nevertheless, the nZVI production on a large-scale still challenges the routines declared above. We made a comparison of these mentioned methods and presented them in Table 1-1.

Table 1-1 The comparison of various preparation methods

Preparation methods	Process	Characteristic
Liquid-phase reduction	Mixing ferrous or ferric ions with $NaBH_4$ to obtain Fe^0 and then the reduced Fe^0 was loaded on supporters like biochar and bentonite.	The most commonly used method, but the additive of $NaBH_4$ is toxic and the post-treatment for effluent is required regulatorily [116].
Mechanical ball milling	Ball milling iron oxides with Al/Zn to produce Fe^0 or ball milling Fe^0 with supporters like AC.	Easily scaled-up for production, but energy consumption is the main concern [117].
Thermal reduction	Reducing iron oxides/hydroxides to Fe^0 through heating under high temperature reducing gas.	Recycling the scrap iron, however, the high energy consumption and the emission of greenhouse gas are the main disadvantages [118].
CVC	Decomposition of $Fe(CO)_5$	The size of Fe^0 particle is adjustable

	under high-temperature inert gas.	by changing temperature, the cost of raw material and energy consumption are the considerations [119].
PED	Preparing Fe^0 by electrochemical reduction.	The purity and thermal stability of prepared Fe^0 are high and the size is controllable, and the power consumption is the central concern [120].
SDR	Introducing $FeSO_4 \cdot 7H_2O$ and $NaBH_4$ solutions into a rotating disk with desired velocity and feeding position to gain Fe^0.	The size of Fe^0 is controllable by adjusting the rotational speed of the disk and the feeding position of solutions [121].

1.1.2.4. Conventional ZVI Composites for Cr(VI) Treatment

1.1.2.4.1 Carbon-ZVI Composites

Biochar, AC, and carbon nanotube have been extensively employed as iron templates to fabricate reliable iron-containing material [122]. Among them, AC possesses stable characteristics because of the developed pores and higher specific surface area, which provided plenty of vacant sites as the iron carrier [123]. Further, AC derived from various kinds of biomass has presented a superior efficiency as a potential adsorbent for Cr(VI) [27, 124, 125]. Moreover, the AC loaded-iron coupled adsorption with reduction has proved to be the main process for Cr(VI) removal [126]. To prepare homogenized AC supported ZVI, the AC was immersed in ferric chloride hexahydrate solution and then was introduced with $NaBH_4$ solution to reduce ferric to ZVI. Finally, nZVI-loaded AC was obtained after centrifugation, filtration, and drying in the nitrogen gas environment

[127]. It was found that the removal efficiency of Cr(VI) increased with an increase in iron loading and the highest removal efficiency (99%) was obtained with the iron loading of 10.9%. On the contrary, the maximum removal efficiency for AC without iron was only 40 %. Further, the characterization of nZVI-loaded AC after treatment has proved that Cr(VI) could be reduced to Cr(III) and precipitated with oxidized product ferric. To illustrate this phenomenon the cyclic voltammetry curve was conducted and was found that it exists the iron-carbon microcell facilitated the redox reaction between iron and Cr(VI).

Similarly, pristine biochar was derived from cornstalk and was modified with H_2O_2, HCl, and NaOH solution. Further liquid-phase reduction method as described above was employed to synthesis iron-loaded biochar and then it was applied for Cr(VI) removal from solution. The Cr(VI) removal experiments results showed that iron-loaded biochar modified with HCl solution exhibited better Cr(VI) removal efficiency than the other two materials. During the process of Cr(VI) removal, the biochar matrix stimulated the redox reaction of iron and Cr(VI) by electrostatic attractions between positively charged biochar and anion chromate, and faded the side impact of Cr(III)/Fe(III) (oxy) hydroxides deposit on the iron particle [128]. Moreover, the micro-galvanic formed between iron particle and carbon matrix contributed to another mechanism, Thus the role of biochar to serve as an electron-transfer mediator through removing aqueous solution Cr(VI) by silicon-rich biochar-supported ZVI was also verified [129]. Compared to iron-loaded on AC or biochar, magnetite-loaded carbon material could endure the defect of secondary separation for by-product [130], owning to magnetic properties of Fe_3O_4 which has attracted much attention for the separation procedure in Cr(VI) removal [131-135]. However, magnetite can easily be inclined to lose magnetic property as a result of oxidation to ferric oxide under acidic conditions [136]. A group of researchers decorated the multiwall carbon nanotube with magnetite nanoparticles and then modified with 1,6-hexanediamine to treat acidic Cr(VI) solution, this synthesized material presented good magnetic property and nearly reached 95%

removal rate of Cr(VI) at pH 2.0 [137]. In addition to the magnetite, γ-Fe_2O_3 had also shown magnetic properties. Laboratory synthesized γ-Fe_2O_3-carbon hybrids could be separated magnetically after the removal of Cr(VI) from the aqueous solution (Fig. 1-5).

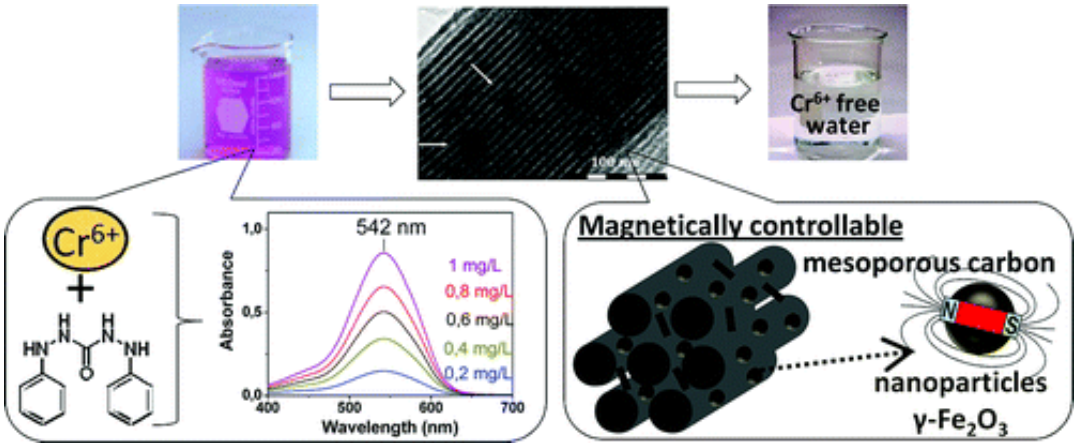

Figure. 1-5 The schematic demonstration of the removal of Cr(VI) by magnetic γ-Fe_2O_3-carbon composite [138], Copyright 2012, ACS Publications.

1.1.2.4.2. Sulfur-ZVI Composites

The reducible species like oxygen, protons [139], and water [140] can consume the electrons originated from ZVI and could damage the utilization efficiency of ZVI to target contaminants. Further, the sulfur compounds modified ZVI could alleviate the unintentional reaction of ZVI with water, and the efficiency of the electron of ZVI could be strengthened as a result. Notably, the findings have demonstrated the essential role of sulfur in the decontamination of trichloroethylene (TCE) [139, 141-143] and florfenicol [144] by S-ZVI. Besides, it has been suggested that sulfur speciation like sulfate radicals specified promising capability on pollutant degradation removal [145]. A team of researchers prepared the S-ZVI composite by mixing the desired amount of iron with elemental sulfur in planetary ball milling within 4 h. Then, the obtained S-ZVI material was employed to treat the Cr(VI) solution under aerobic conditions. The S-ZVI composites appreciably increased the electron effectiveness of iron to Cr(VI) which was 10.7-fold higher than bare iron. The enhancement effect of sulfur species was

mainly ascribed to the FeS, which boosted the attachment of chromate onto the surface of S-ZVI and transferred the electrons to chromate [146]. Similarly, the aqueous Cr(VI) was eliminated by S-nZVI composites with a higher S/Fe molar ratio [147], and the removal process has been demonstrated in Fig. 1-6. Based on the prior literature about pollutants elimination by iron under aerobic and anaerobic conditions, it was observed that undesirable hydrogen evolution reaction between iron and water also depleted iron under anaerobic condition, thus decreased the longevity and electron selectivity of iron [148-152]. A comparison between bare iron and sulfur-modified iron was also executed, it was found that the latter implied conservative hydrogen production rate and amount [153]. A plausible explanation for the suppressed reactivity of ZVI to water was that the sulfur-modified ZVI inclined to hydrophobic and the reaction of hydrogen evolution from ZVI and water was mitigated as a result. It made sulfur-modified iron a potential material for anaerobic groundwater remediation. Recent cases also supported the hypothesis that sulfur could fascinate the selectivity and activity of iron to the targeted pollutants [154]. It has been demonstrated that S-nZVI fixed with carboxymethyl cellulose (CMC) presented higher mobility and stability in the sub surfaces for field applications [155].

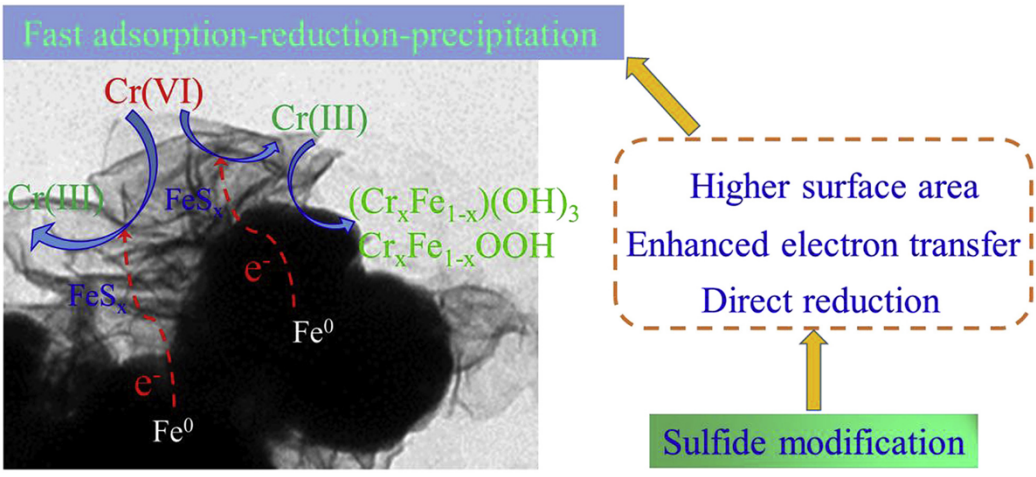

Figure. 1-6 Removal of aqueous Cr(VI) by S-nZVI. The increased surface area after modified with sulfur fascinated the adsorption of Cr(VI), and the FeS_x favored the corrosion of ZVI to target Cr(VI) [147], Copyright 2019, Elsevier.

1.1.2.4.3. Bimetallic Composites

Previous studies have defined bimetal of iron as incorporating the second metal such as Al, Ni, Pt, Ag [156] and Pd [157], Cu [158] with iron. The chemical and electronic properties of the bimetallic materials are optimized evidently as compared to the solitary metals [159]. Table 1-2 is illustrating a summary of the published reports on Cr(VI) removal by ZVI-based bimetallic materials. The main drawback of the bimetallic materials is the employment of noble metals like Ag and Pt or the use of toxic metals such as Ni and Cu as second metals. However, it makes the rarely available metals to fabricate bimetal of iron for pollutants remediation in the large-scale application. Al as the most abundant metallic element on the earth was an ideal candidate for Al-Fe preparation. Besides, the elemental Al has been extensively employed for the removal of a variety of pollutants such as Cr(VI) [160-163], bromate [164], TCE [165] and phenol [166]. The Fe-Al bimetallic particles were fabricated via depositing iron on the Al surface for Cr(VI) removal. The desired mass of Al was added to deionized water, which was priorly mixed with the desired concentration of $FeSO_4$ solution. Then it was rinsed and dried after stirred for 30 min. Different ratio of Al/Fe was obtained by regulating the dose of Al and Fe, the synthesized Fe-Al material was the Al-cored particle and Fe was deposited on its outer layer. The galvanic cell based on Fe as anode and Al as cathode for the electrode potential of Fe (-0.44V) was higher than Al (-1.67V). For this reason, the Cr(VI) was reduced by electrons donated by the Al core and transferred through the iron shell. The iron accelerated the electrons transfer from Al to Cr(VI) and higher removal efficiency was achieved over a wide range of pH (3.0 to 11.0) [72]. Similar studies of the galvanic effect of Al-Fe bimetallic particles for Cr(VI) elimination from aquatic environments was conducted by [167]. In contrast to earlier findings, however, Al-Fe bimetallic that ZVI coated with zero-valent Al has shown lower Cr(VI) removal capacity. However, another research team found that Fe/Al bimetallic material has demonstrated 21 folds higher Cr(VI) removal efficiency than Al/Fe bimetallic [168]. It

was due to the oxidation of the Al layer by Cr(VI). Then, the electrons from Al and ZVI was quarantined from contaminants, but concerning iron-coated Al particle, the pathway of electron transfer from Al to Fe was unaffected by contaminants. The oxidized Fe^{2+} by Cr(VI) could be reduced to Fe^0 by Al spontaneously. A similar galvanic cell effect on Fe/Co bimetallic has been demonstrated in Fig. 1-7.

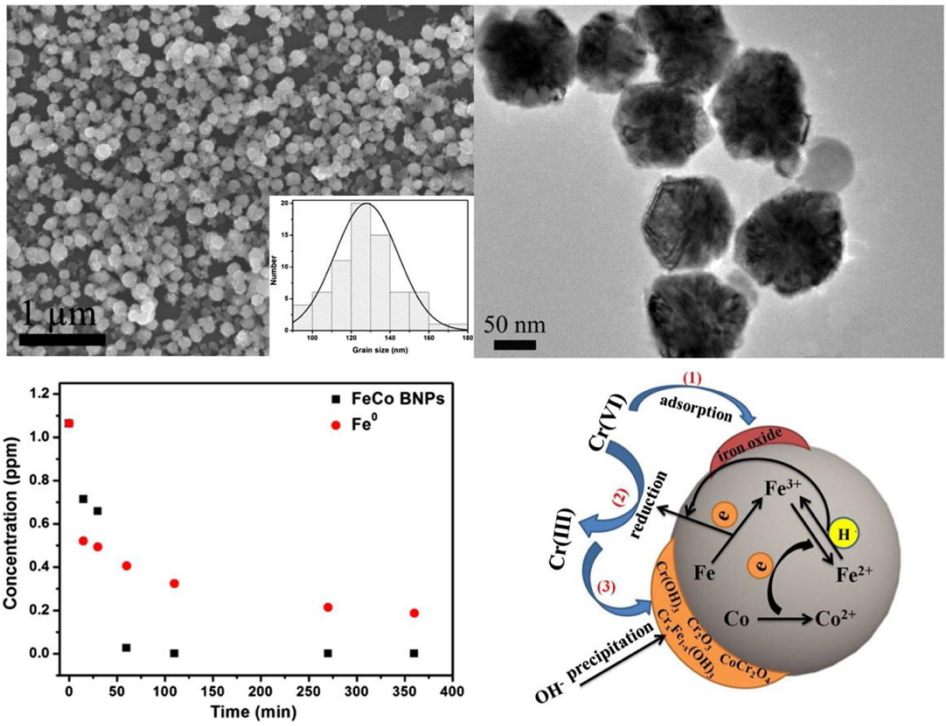

Figure. 1-7 The removal process of Cr(VI) by Fe-Co bimetallic coated by tea-polyphenol. The removal efficiency enhanced after incorporated with Co, ZVI was depleted by Cr(VI) and the Co can maintain the activity for ZVI that electron derived from Co can reduce Fe^{3+} to Fe^{2+}. The reduced Cr(III) separated from the solution by precipitated as $Cr(OH)_3$ and $Cr_xFe_{1-x}(OH)_3$ with Fe^{3+} [169], Copyright 2016, Elsevier.

As compared to the laboratory scale liquid reduction method, the melting and ball milling techniques for synthesis of bimetals exhibited higher homogeneity, superior mechanical stability, and greater potential in large-scale applications [170-173]. Typically, the desired ratio of Al and Fe powder in MgO crucible is melted in a vacuum melting furnace, and then the obtained Al-Fe was crushed into particles for further applications in the removal of targeted contaminants [173]. It was noticed that Al-Fe particles

consisting of 20% Fe prepared through melting method has indicated favorable removal performance of Cr(VI) [174]. According to the available literature, ball milling is the most widely used mechanical procedure for the preparation of bimetallic materials for pollutants elimination [175-178]. The bimetallic materials produced by ball milling have demonstrated some advantages, such as simple operation, easy scaling up, and time-saving. However, as far as we know, most of the researches up till now did not focus on the preparation of Fe-Al particles through high energy ball milling, thus, the study would be more beneficial if a wider range of ball milling procedure for Fe-Al preparation is explored, especially for Cr(VI) eradication.

Table 1-2 ZVI-based bimetallic materials for Cr(VI) removal

Bimetals	Synthesis methods	Reducing agents	Removal (%)	Operational pH	Removal mechanism	Refs(s)
Ni-ZVI	Liquid-phase reduction	KBH_4	96.33-60.31	2.0-7.0	Reduction, adsorption, and precipitation	[179]
Ni-ZVI	Liquid-phase reduction	$NaBH_4$	100	1.0-3.0	Reduction, adsorption	[180]
Mont-supported Ni-ZVI	Liquid-phase reduction	$NaBH_4$	100	1.0-3.0	Reduction	[180]
Ni-ZVI	Chemical vapor deposition	H_2	83	N/A	Reduction, adsorption	[181]
Cu-ZVI	Liquid-phase reduction	$NaBH_4$	50.57	2.0	Reduction, adsorption	[182]
Pd-ZVI	Liquid-phase reduction	$NaBH_4$	95.5-73.0	3.0-8.0	Reduction, adsorption, and precipitation	[183]
Cu-ZVI	Liquid-phase reduction	Extract of green tea	94.7	5.0	Reduction, adsorption, and precipitation	[184]
Cu-SZVI	Liquid-phase reduction	Fe	97.9	8.0	Reduction	[185]
Al-Fe	Liquid-phase reduction	Al	90.0	7.0	Reduction, Precipitation	[167]

N/A. Not available

1.1.2.4.4. Magnetite-ZVI Composites

Magnetite or ferrosoferric oxide (Fe_3O_4) is commonly found in nature and characterized by properties like conductivity, magnetism, high surface area, and reducibility. Its importance in literature has been recognized in the elimination of targeted contaminants [71, 186-192]. It was reported that Cr(VI) could directly reduce by magnetite [193]. Further, the coupling of magnetite with iron for the degradation/reduction of contaminants would not only accelerate the corrosion of iron but also easily separate from aqueous solutions [194-196]. The structural Fe^{2+} of magnetite can act as an electron channel from iron to pollutants. Briefly, Fe^{2+}(s) in the octahedral site of magnetite could be oxidized by targeted contaminants to Fe^{3+}(s), and then the oxidized Fe^{3+}(s) could be reduced back to Fe^{2+}(s) by accepting electrons from Fe^0 and this process is thermodynamically favorable, as suggested by standard electrode potential, which is expressed as in Eq (1-5) [197], and without construal constrain [198, 199]. Regarding this, Fig. 1-8 is showing synergistic effects of Fe_3O_4/Fe on Cr(VI) removal.

$$2Fe^{3+}(aq) + Fe^0(s) = 3Fe^{2+}(aq) \quad \Delta E^0=1.21V \qquad (1\text{-}5)$$

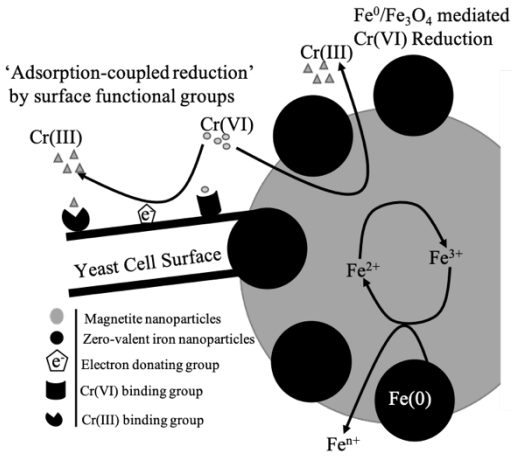

Figure. 1-8 The Yarrowia modified Fe_3O_4-Fe^0 employed for Cr(VI) elimination. The oxidized Fe^{3+}(s) from Fe_3O_4 by Cr(VI) converted to Fe^{2+} (s) by Fe^0 [200200], Copyright 2013, Elsevier.

To determine the effect of Fe^{2+}(s) of magnetite on Cr(VI) removal by Fe_3O_4-Fe^0, the removal performances of Fe^0-α-Fe_2O_3, Fe^0-γ-Fe_2O_3, and Fe^0-FeOOH were compared with Fe^0/Fe_3O_4. The Fe^0/Fe_3O_4 composite depicted a higher Cr(VI) conversion rate (65%) as compared to the other three composites. In contrast, the bare Fe^0 and Fe_3O_4 only converted 15% and 25% Cr(VI), respectively [201]. Moreover, the conventional Fe^0/Fe_3O_4 composite failed to consider the long-term impact of neutral or alkaline conditions. For instance, the Cr(VI) removal efficiency by Fe^0/Fe_3O_4 composite dropped significantly from 100% to 35.88 % as pH increased from 7 to 10 [202]. Furthermore, a previous study reported that the reduction of aqueous Cr(VI) by magnetite was ceased after 10-20 Å surface of magnetite was oxidized into maghemite (γ-Fe_2O_3) at pH 7.0 [203]. It was might be due to the surface passivation effect. Recently, a hydroxyl-modified Fe^0-Fe_3O_4 was fabricated with the addition of Na_2EDTA complexation, and then it was employed for the removal of Cr(VI). The results indicated that the concentration of Cr(VI) was lessened continuously, which could be attributed to the contribution of complexation of Na_2EDTA with Fe^{3+} and Cr^{3+} [178]. Moreover, the EDTA ligand assisted sequestration procedure has gained much attention presently due to its cost-effectiveness and its outstanding capability in the elimination of various contaminants like heavy metals, organic matters, etc. [204-209]. Nevertheless, the existing accounts have failed to resolve the contradiction between in-situ application and environment protection, the degradation of EDTA is important before its discharging to prevent the environment from EDTA toxicity [210]. Thus, more research efforts would be required to find out eco-friendly ligands which can assist the removal of Cr(VI) from the environment by Fe^0/Fe_3O_4 composites.

1.1.2.5. Mechanism of Cr(VI) Sequestration by ZVI-based materials

The route of Cr(VI) removal by ZVI-based materials is mainly controlled with the combination of reduction, adsorption, and co-precipitation, wherein the leading reduction process is effected essentially by pH and DO. The reduction capacity of

pristine iron was inhibited due to the intrinsic defect caused by the passivation layer under alkaline and aerobic/anaerobic conditions. The resulting constitution of ZVI after treating with Cr(VI) could clearly be described by two linear dimensions [211]. Deliberately formulated ZVI-based materials have been used to preclude the passivation on the surface of ZVI to promote the electron efficiency and permanence of iron. In the current review, we predominantly consider the mechanism of encouraged Cr(VI) reduction potential of ZVI after incorporated into AC/biochar-ZVI, ZVI-based bimetal, sulfur-ZVI, and magnetite-ZVI composites.

The effect of the galvanic cell has been evidenced to be the main path for Cr(VI) reduction by AC-supported iron [212] and ZVI-based bimetal [213]. The electrons derived from ZVI could be transferred to the target contaminant via AC and the corrosion of ZVI was facilitated, consequently. The produced secondary reductant Fe^{2+} accompanied with the oxidation of Fe^0 could further reduce Cr(VI), and the Cr(III) could be precipitated with Fe^{3+} because the improved pH of the aqueous solution was initialed by redox couple of Cr(VI)-Fe^0/Fe^{2+}. Moreover, the adsorption property of AC on Cr(VI) could advance the reduction process.

Based on the reduction potential difference between Fe^0 and another metal in the bimetallic pair, Fe^0 could serve as an anode in the galvanic cell when coupling with less active metal and could also act as a cathode instead when coupling with the higher active metal [214]. The electrons transported directly from anode Fe^0 or indirectly through less active metal to contaminant, this pathway was greatly related to the configuration of ZVI-based bimetallic particles. In general, these two electron relocation channels were both driven by reduction potential difference of Fe^0-pollutants or Fe^0-Cu/Ni couples when Fe^0 dispersive homogeneously in bimetallic [215, 216]. The electrons originated from the Fe^0 core could simply be transferred indirectly through inert shell metal like Cu or Ni to Cr(VI), conversely. And the core-shell structure could deteriorate the undesirable effect of the passivation layer on Fe^0 [158, 217]. The effect of Cu layer on iron endurance to contaminant transformed from positive to negative when increased

the mass of planting Cu on the iron core from heterogeneous and loose to dense and uniform film, owing to the galvanic corrosion of Fe-Cu was readily formed with loose Cu layer [218]. While Fe^0 performs as a cathode in bimetallic material, the reduction of contaminants arisen from three kinds of electron transportations; electrons from Fe^0, higher active metal (e.g., Al), and the galvanic cell of bimetallic [219]. Fe-Al bimetallic prepared by liquid reduction method or replacement reaction suggested a desirable Cr(VI) removal efficiency over a wide pH range (3-11), three electron assignment paths mentioned above contributed appreciably to the Cr(VI) reduction and the subsequent precipitation removal [72].

The reduction of Cr(VI) by sulfur-modified ZVI involved two phases, Cr(VI) reduced directly by Fe^0 and indirectly by the regenerated Fe^{2+} from redox of Fe^{3+}/Fe^0 couple [220]. The sulfured iron film on the surface of the iron core could enhance the corrosion of Fe^0 via the electron transfer from Fe^0 to oxidized Fe^{3+}. Meanwhile, the Cr(VI) reduction performance would be un-favored once excess sulfur was introduced as the core Fe^0 would be covered by a dense sulfidation iron layer [221]. It was also found that the regeneration of Fe^{2+} was absent in the reduction of Cr(VI) by excess sulfur modified iron, it can inference that the iron core was overlaid completely by the outer FeS layer and constrained the regeneration of Fe^{2+} from soluble aqueous Fe^{3+} [222]. Besides, the surface area of iron increased after the sulfidation, which helped in the adsorption of Cr(VI) and succeeding reduction. Corresponding to the passivation of ZVI, the virgin magnetite was also expected to be passivated with maghemite, goethite, and/or $Cr_{1-x}Fe_xOOH$ under alkaline pH during reaction with Cr(VI) which inhibited the reduction of Cr(VI), subsequently [71]. Similarly, a research study implied that the removal efficiency of Cr(VI) on magnetite-ZVI composite was 96.4 %, while about 18.8 % and 48.8 % were noticed by ZVI and Fe_3O_4, respectively [202]. It speculated that the regeneration of Fe^{2+} in magnetite sponsored the enhancement of Cr(VI) sequestration in magnetite-ZVI composite compared to bare ZVI [223]. The octahedrally located Fe^0 on Fe_3O_4 cycled the oxidized Fe^{3+} in magnetite to Fe^{2+} for the further

reduction of Cr(VI) with Fe^0. The enhancement of electron selectivity of Fe^0 to Cr(VI), acceleration of corrosion of Fe^0, and the regeneration of Fe^{2+} are the main mechanisms that contribute to the superior Cr(VI) removal capacity by ZVI-based materials. The effect of galvanic cell and the conductive layer covered on Fe^0 accelerate the electron transfer from Fe^0 to Cr(VI), particularly.

1.1.2.6. Comparison with others iron-based materials

The Fe(II)-containing minerals such as pyrite (FeS_2), ferrous sulfide (FeS), and green rusts (GRs) established promising properties on the environmental remediation technologies [224-226]. The GRs as the layer structured Fe(II)-Fe(III) hydroxides possessed an outstanding competence on pollutants reductive removal owing to having a higher content of Fe(II). Meanwhile, the GRs were unstable and the stability modification was essential to lengthen the endurance. Green rust chloride immobilized with silicate (Si), phosphate (P), fulvic acid (FA), CMC, and bone char (BC) were used for Cr(VI) removal, and the results indicated that the release of Fe(II) was retarded after immobilization and fast removal of Cr(VI) was noticed by using over 90% of Fe(II) [227]. Bae et al., (2020) studied the capacity of Fe(II)-phosphate mineral (i.e., vivianite) on Cr(VI) removal, it found that Cr(VI) was reduced by structural Fe(II) in vivianite and then formed a complex with the generated mixed-valence Fe-phosphate [228]. Recently, the FeS_2 particles presented an effective Cr(VI) eradication over a wide pH range (6.0-9.5) [229]. To reinforce the removal of Cr(VI), the FeS-loaded titanate nanotubes were prepared hydrothermally, the Cr(VI) was reduced efficiently by FeS and the produced Cr(III) was adsorbed on titanate nanotubes simultaneously [230]. In general, a wider scope of iron-based materials that are not limited to ZVI-based materials or Fe(II)-containing minerals would help us to extend the application of iron-based materials on Cr(VI) sequestration.

1.1.3. The governing conditions for ZVI performance

1.1.3.1. pH

The speciation and oxidation states of Cr(VI) are greatly dependent on the value of solution pH. The species of Cr(VI) in aqueous solution consists of chromic acid (H_2CrO_4), bichromate ion ($HCrO_4^-$), chromate ion (CrO_4^{2-}), and dichromate ion ($Cr_2O_7^{2-}$), to illustrate the formation process of Cr(VI) complexes, the equations can be seen in Eqs (1-6)-(1-8) [231].

$$CrO_4^{2-} + H^+ = HCrO_4^- \qquad pK_1=6.51 \qquad (1\text{-}6)$$

$$CrO_4^{2-} + 2H^+ = H_2CrO_4 \qquad pK_2=5.65 \qquad (1\text{-}7)$$

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O \qquad pK_3=14.56 \qquad (1\text{-}8)$$

The speciation of hexavalent chromium (1000 ppm) as a function of pH was calculated based on the value of pK, the Fig. 1-9 reveals that the predominant species of Cr(VI) are $HCrO_4^-$ and CrO_4^{2-} which exists at below pH 5.0 and up to pH 8.0, respectively.

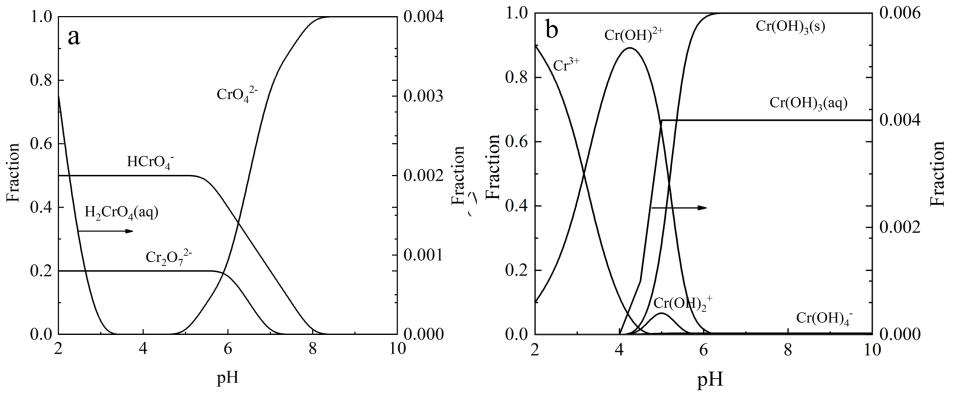

Figure. 1-9 Speciation diagram of (a) Cr(VI) and (b) Cr(III) at different pH

Further, the half-cell reactions of Cr(VI) under acidic and alkaline conditions are expressed as in Eqs (1-9)-(1-10), respectively [232]. Acidic solution favors the oxidation state of Cr(VI), on the contrary, Cr(VI) presents the least significant oxidation state under neutral and alkaline conditions. It was demonstrated that the reduction rate of Cr(VI) by Fe^0 increased notably for near 20 times from pH 7.5 to 5.5, and a negligible Cr(III) was detected after pH increased to 8.0. While, the logarithmic value of the first-order rate coefficient of Cr(VI) removal as a function of pH value is highly linear fitted which the slope is 0.72 ± 0.07 [233]. Further, a team of researchers stated that their data

strongly supported the view of Alowitz et al. (2002) that the H^+ accelerated the corrosion of iron and promoted the Cr(VI) reduction. It was found that the removal efficiency of Cr(VI) was significantly declined from 97 % to 50 % as pH increased from 4.0 to 10.0 [234].

$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ E_0=1.36V (1-9)

$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_4^- + 4OH^-$ E_0=-0.13V (1-10)

$Fe^0 + HCrO_4^- + 7H^+ = Fe^{3+} + Cr^{3+} + 4H_2O$ Acidic conditions (1-11)

$Fe^0 + CrO_4^{2-} + 2H_2O = Fe^{3+} + Cr^{3+} + 4OH^-$ Alkalic conditions (1-12)

It should be noted that redox reactions between Fe^0 and Cr(VI) (Eqs (1-11)-(1-12)) were varied substantially as pH. Furthermore, the pH of the solution will increase as the redox reaction carried on either due to the protons consumed or hydroxyl ions (OH^-) generated. Referred to the theory of point of zero charge (pzc), the material presents the positive charge when the pH of the aqueous solution is below the pH of pzc (pH_{pzc}), it exhibits the negative charge when solution pH surpasses the value of pH_{pzc}, conversely [235]. Previously the pH_{pzc} value of ZVI was reported around 7.7-8.3 [236-239]. Thus, it can be concluded that ZVI will be negatively charged at pH over 8.3 and the transport of anion chromate in bulk solution to ZVI surface will be inhibited due to electrostatic repulsion.

To further demonstrate the alkaline condition post side effect on Cr(VI) removal, nano-ZVI was synthesized by the liquid reduction method and was applied for Cr(VI) elimination. It was observed that the removal rate of Cr(VI) decreased around 3-fold from pH range 3.0-4.0 to pH 9.0, meanwhile, the pH of the solution was increased from 3.0 to 6.2 within 60 min [240]. Contrary to the previous findings that increasing pH has a post negative effect on Cr(VI) removal, however, the removal efficiency of Cr(VI) was higher at pH 5.0 under Fe^0/H_2O system between pH 4.0 and 6.0. Comparing to pH 5.0, iron showed a higher reduction capacity at pH 4.0 but the reduced product of Cr(III) was soluble and remained in solution. Furthermore, at pH 6.0, the reduction rate of Cr(VI) was declined greatly due to the minor availability of free protons [85]. Here, the

major source of uncertainty is the applied method for the evaluation of the removal performance of Cr(VI) by iron. Generally, the removal mechanism includes the combination of reduction, adsorption, and co-precipitation. Regarding monometallic iron, the removal was mainly contributed by reduction and adsorption at acidic conditions, reduction and co-precipitation under neutral or alkaline conditions. Most accepted equations for removal capacity of Cr(VI) can be seen in Eqs (1-13)-(1-14).

$$q_1=(c_0-c_{Cr(VI)})/c_0 \quad (1\text{-}13)$$

$$q_2=(c_0-c_{total\ Cr})/c_0 \quad (1\text{-}14)$$

Wherein, q_1 and q_2(mg/g) are the removal capacity, c_0(mg/L) is the initial concentration of Cr(VI), $c_{Cr(V)}$ and $c_{total\ Cr}$ (mg/L) are the concentrations of Cr(VI) and total chromium (Cr(VI), respectively. For the Eq (13), it was observed that the value of q_1 decreases gradually as the increase of pH because of the drop of Cr(VI) reduction rate, whereas the variation of q_2 as pH was affected by Cr(VI) and the reduced product Cr(III) for the Eq (14). In brief, reduced soluble Cr(III) decreased gradually as pH increase and started to precipitate when pH over 5.0, and the residual concentration of Cr(VI) increased as pH. Therefore, the value of q_2 was not linearly related to pH. This illustrated the optimal pH for the removal of Cr(VI) by Fe^0 was not the lower value when employed Eq (14). Although extensive research has been carried out to assess the capability of iron for Cr(VI) elimination, however only a few researchers have been able to draw a systematic approach [241-245]. Thus, it was found that a much more systematic approach would result in the identification of reduction and removal capability of iron, a complete removal process should involve the conversion of Cr(VI) to Cr(III) and the final separation of Cr(III) from solution.

1.1.3.2. Dissolved Oxygen

The erosion of iron is highly affected by dissolved oxygen (DO) in aqueous solution, the oxidation product can be seen in Eqs (1-15)-(1-17), it was demonstrated that in the presence of a high concentration of DO in solution, ferrous ion (Fe^{2+}) can be further

oxidized to ferric ion (Fe^{3+}) and then could be precipitated with hydroxide (OH^-) [246]. While, Fe^0 is reported as an effective reductant for Cr(VI) [247, 248].

$$2Fe^0 + O_2 + 4H^+ = 2Fe^{2+} + 2H_2O \quad (1\text{-}15)$$

$$4Fe^{2+} + 4H^+ + O_2 = 4Fe^{3+} + 2H_2O \quad (1\text{-}16)$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3(s) \quad (1\text{-}17)$$

It was documented that iron erosion under anaerobic implies a slower rate than that under aerobic, as shown in the Eqs (1-18)-(1-19), due to the formation of ferrous (oxy) hydroxides ($Fe(OH)_2$) instead of ferric (oxy) hydroxides (FeO(OH)). It was found that $Fe(OH)_2$ remained stable in free oxygen and at low temperature [150, 249].

$$Fe^0 + 4H_2O = Fe^{2+} + 2H_2 + 4OH^- \quad (1\text{-}18)$$

$$Fe^{2+} + 2OH^- = Fe(OH)_2(s) \quad (1\text{-}19)$$

In general, oxygen may compete for the available sites and electrons of iron with contaminants like Cr(VI) and reduce the efficiency of the electron. On the other hand, the desired concentration of DO stimulated the generation of soluble Fe^{2+} and promoted the elimination of pollutants [250].

The Fe^{2+} was stable under acidic conditions in the presence of oxygen but could easily be oxidized by oxygen under alkaline conditions. The reaction kinetics of Fe^{2+} with Cr(VI) under pH 2.0 was higher than those under pH 6.0 for two orders of magnitude [246, 251, 252]. It meant that Fe^{2+} predominant the redox reaction with Cr(VI) under acidic solution in the presence of oxygen. To further demonstrate the role of Fe^{2+} on Cr(VI) removal under acid/anaerobic solution, 1,10-phenanthroline was introduced as a populated indicator for Fe^{2+} into Cr(VI)/Fe^0 system to complexes strongly with Fe^{2+}. Hence, the availability of Fe^{2+} to Cr(VI) was inhibited, and the results indicated that the removal of Cr(VI) was substantially suppressed in the presence of 1,10-phenanthroline [220]. Similar reports were also supported this idea by adding 1,10-phenanthroline to isolate Fe^{2+} from acid/anaerobic aqueous solution [204, 221, 253]. The generated Fe^{2+} abound in bulk solution which verified by the results that removal rate of Cr(VI) impeded after introducing 1,10-phenanthroline complex. Notably, the data from several sources have

identified that the increase in removal performance of Cr(VI) resulted from the produced Fe^{2+} under oxic solution that associated with the Fe^0 surface-bound with Fe^{2+}, not just the free Fe^{2+} in bulk solution [220, 254].

The reduction product of Fe^0 in Cr(VI) solution favors forming the γ-FeOOH or α-FeOOH over α-Fe_2O_3 or γ-Fe_2O_3 [255-257]. Wherein the iron oxyhydroxides (goethite and lepidocrocite) had shown relatively high specific surface, and the reduced Cr(III) could easily be adsorbed on them [258]. The iron oxyhydroxides incorporated with Cr(III) could further transform to sparingly soluble $Cr_xFe_{1-x}(OH)_3$ [259, 260]. This claim has been completed by many researchers [85, 261, 262]. Briefly, it was found that the product was different under oxic and anoxic conditions of Fe^0/Cr(VI) setup, meanwhile, the removal efficiency under oxic was much better than those under anoxic conditions. The porosity of the $FeCr_2O_4$ layer was predominantly covered on iron under oxic/acidic conditions, while the compact layer of hydroxide/oxyhydroxides of Fe(III) and Cr(III) was produced under anoxic/acid condition. The redox product of $FeCr_2O_4$ under oxic/acid conditions substantially coincided with the product of Fe^{2+} and Cr(VI) [263]. It can be concluded that the governing mechanism for Cr(VI) removal by iron under oxic/acid conditions was due to the generation of Fe^{2+} from iron with oxygen and then reacted with Cr(VI).

A recent study concluded a converse view that $FeCr_2O_4$ was formed under anoxic/acid condition, while the iron/chromium oxyhydroxides appeared in the presence of oxygen under acid condition, nevertheless, the presence of oxygen impaired the removal rate of Cr(VI) by iron [240]. The most likely cause of either positive effect or negative effect of DO on Cr(VI) removal under acid condition was the transformation of redox product of Fe^0/Cr(VI) with DO concentration. Typically, the desired amount of oxygen could accelerate the corrosion of iron and the generation of reductant Fe^{2+} accompanied with reserved protons depletion, and the Cr(VI)/Fe^{2+}(aq) and Cr(VI)/Fe^{2+}(s) (bounded on Fe^0) couples could generate loose $FeCr_2O_4$. Adversely, the excess oxygen could deteriorate the effectiveness of iron through further oxidation of Fe^{2+} to Fe^{3+} by

Fenton reaction [264], and the consumed protons could produce compact $Cr_xFe_{1-x}(OH)_3$, simultaneously. Thus, more efforts are required to find the exact critical value of DO concentration. Previous studies about oxygen influence did not focus on its concentration in solution, and most of the attempts were made to compare the aerobic and anaerobic by aeration with oxygen or nitrogen gas [265, 266]. Furthermore, the passivation layer composed of hydroxide/oxyhydroxides of Fe(III)/Cr(III) on the surface of iron hindered the electrons transfer from iron to Cr(VI) under over oxygen content [83]. The shielding effect of the passivation layer formed in the presence of oxygen is evidenced [254].

Altogether, the effect of DO on Cr(VI) removal by ZVI was not only dependent on solution pH but also relied on its concentration. It could be divided into the following five pathways: (1) The important intermediate reducing agent Fe^{2+} that originates from Fe^0 contributed to the elimination of Cr(VI) under lower DO and acidic conditions; (2) the higher value of DO under acid conditions could oxidize immoderately Fe^{2+} to Fe^{3+} and weaken the electron efficiency of Fe^0; (3) under anaerobic/acid conditions, the protons accelerated the erosion of Fe^0 and the produced Fe^{2+} could participate in the reduction of Cr(VI); (4) Due to the instability of Fe^{2+} under aerobic/alkaline conditions and the generated compact precipitate covered on the Fe^0, and the durability of Fe^0 deteriorated accordingly; (5) The Fe^0 and the produced Fe^{2+} both were involved in the reduction of Cr(VI) in the deficiency of DO under alkaline conditions, which improved the removal efficiency of Cr(VI). The specific information about the co-effect between DO and pH is shown in Table 1-3.

Table 1-3 The co-effect of DO and pH on Cr(VI) removal by iron

Operation conditions	Aerobic/acid		Anaerobic/acid	Aerobic/alkaline	Anaerobic/alkaline
	Low DO	High DO			
Effect	Strengthen the performance of iron	Deteriorate performance of iron	Strengthen the performance of iron	Deteriorate performance of iron	Strengthen the performance of iron
Mechanism	$2Fe^0 + O_2 + 4H^+ = 2Fe^{2+} + 2H_2O$ $Fe^0 + HCrO_4^- + 7H^+ = Fe^{3+} + Cr^{3+} + 4H_2O$ $Fe^{2+} + HCrO_4^- + 7H^+ = Fe^{3+} + Cr^{3+} + 4H_2O$	$4Fe^0 + 3O_2 + 12H^+ = 4Fe^{3+} + 6H_2O$	$Fe^0 + 2H^+ = Fe^{2+} + H_{2(gas)}$ $3Fe^{2+} + HCrO_4^- + 7H^+ = 3Fe^{3+} + Cr^{3+} + 4H_2O$ $Fe^0 + HCrO_4^- + 7H^+ = Fe^{3+} + Cr^{3+} + 4H_2O$	$2Fe^0 + 2H_2O + O_2 = 2Fe^{2+} + 4OH^-$ $4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^-$	$Fe^0 + 4H_2O = Fe^{2+} + 2H_2 + 4OH^-$ $Fe^0 + CrO_4^{2-} + 2H_2O = Fe^{3+} + Cr^{3+} + 4OH^-$ $3Fe^{2+} + CrO_4^{2-} + 4H_2O = 3Fe^{3+} + Cr^{3+} + 8OH^-$

1.1.4. Practical Applications of ZVI-based materials

Since it was reported in 1925, permeable reactive barrier (PRB) is attracting a lot of interest in the remediation of groundwater pollutants such as organic matters, heavy metals, inorganic matters [267, 268]. It was recorded in 2009 that there were 13 full-scale PRB present worldwide. From them, 6 PRBs were equipped with ZVI as reactive media [269]. The field-scale of PRB was operated under more complicated conditions as compare to the laboratory-scale, such as they did face fairly slow flow, low dissolved oxygen, relatively high pH value, lower temperature, low contaminants concentration, and a range of inorganic anions like CO_3^{2-}, SO_4^{2-}, NO_3^{-} [270, 271]. In the laboratory studies, the principal mechanism for Cr(VI) removal by ZVI-PRB was presumed to be the redox reaction between Cr(VI) and Fe^0, which could be undermined by the formation of insoluble Fe(III)/Cr(III) (oxy) hydroxides phase [272]. While the removal process for Cr(VI) under field sites would be uncertain owning to the other competitive ions. In general, more attempts are needed to transfer laboratory-based theory to field-scale application.

Longevity and reactivity are the two major considerations in the long-term operation capability of PRB [273]. An early example of research into the reactivity of ZVI PRB has demonstrated that the intensively reducing process and high pH value could be associated with the diminish of reactive media due to the precipitation of inorganic species, which consequently clogged the permeable pore of PRB [274]. Further, about 0.88%/year decline in porosity of ZVI PRB was noticed, which hinted that the loss of carbonates (90%), calcium (82%), and sulfate (69%) in groundwater flow through the PRB [275]. Moreover, the column experiments with various groundwater geochemistry for sequestration Cr(VI) through ZVI were also investigated to elucidate the effects of hardness and carbonate on Cr(VI) removal by ZVI in groundwater, and their results indicated that the capability of ZVI dropped slightly in the presence of calcium hardness. Notably, the Cr(VI) removal capacity of ZVI decreased by 17% under magnesium solution. Furthermore, it was found that a 33% decrease in ZVI performance was

noticed in the co-present of hardness and carbonate in columns [276]. Similar research implied the bicarbonate gave the mildest impact on Cr(VI) removal by ZVI compared to calcium, magnesium ions, whereas bicarbonate together with calcium posted the greatest impact on ZVI efficiency for Cr(VI) removal [277]. On the other hand, not all deposits on the barrier are unfavorable for the reactivity of ZVI media, the ferrous precipitates like magnetite and green rust could transfer electrons from ZVI to pollutants [278, 279]. It can therefore be assumed that the permeability of PRB could drop gradually due to the formation of precipitate on the surface of ZVI particles, but the reactivity of ZVI could either reduce or enhance with time, which can be correlated with the geochemical conditions of groundwater like DO and pH.

The longevity of ZVI PRB could be referred to as its potential to maintain the reactivity of filling media and hydraulic performance, while the hydraulic performance was related to the residence time of plume pass through the barrier [280]. Construction methods, reactive material, and groundwater constituents affected the life cycle of PRB. The data from several sources have identified that the trench-based construction method showed significant remediation capacity on Cr(VI) compared to the caisson-based construction method. Notably, the ZVI and iron oxide-coated sand could reduce the environmental impact on PRB. Natural organic matters (NOM) in groundwater could lower the PRB capability due to the depletion of the higher amount of ZVI [281]. For instance, no significant reduction in the performance of PRB was observed even after continuous operation for 13 years [61, 282].

In contrast, the study of Bronstein, et al (2005) noticed a significant fluctuation in the removal performance of Cr(VI) after the operation of one year [283]. Thus, It has been presumed that the uneven depletion of ZVI in plume could decline the longevity in the PRB over time [284]. Apart from the study aimed at the construction method, groundwater constituents, and media reactivity, more comprehensive hydrology of groundwater should be examined. Therefore, the contaminants concentration distribution and flow velocity changes should be taken into account for PRB design and installation. Besides the bare ZVI used for PRB reactive media, the ZVI-based materials like S-nZVI and

nZVI-SBA-15 have been developed as the substitute material for Cr(VI) isolation in groundwater at pilot-scale or field trials [285, 286]. Compared to single ZVI, ZVI-based materials could prevent the reactivity loss of nZVI that results from congregating. Various surveys have shown that the permeable reactive columns filled with activated carbon fiber supported nZVI have exhibited a higher Cr(VI) removal efficiency [287]. Therefore, more research efforts are needed in this direction for shifting ZVI-based materials PRB from laboratory-based data to practical implantation.

Moreover, the injection well technology is another most used method excluding PRB technology for groundwater remediation [288]. The media particles were prepared as slurry before injecting into the polluted source sites or plume, in which the extensively utilized media are ZVI and bimetallic particles of iron [271]. Remarkably, the Cr(VI) concentration declined substantially from 4-8 mg/L to 0.015 mg/L by employing a composite of ferrous sulfate (Fe_2SO_4) combined with sodium dithionite ($Na_2S_2O_4$) as the reactive media in the injection well [289]. Sodium dithionite could prevent the premature oxidization of Fe^{2+}, and could prevent the clogging of injected media, and maintained effective hydraulic conductivity. Similarly, an over 96% degradation ratio of TCE was noticed by injecting bimetallic particles of Fe-Pd gravitationally into the groundwater [290]. The particles were supplied at an optimal rate, which presented ideal mobility and diffusion. However, the in-site remediation cases all required the ZVI-based materials prepared on the spot, for example, the CMC-stabilized Fe-Pd composite was synthesized on the site through liquid reduction right before injection into the wells to minimize the reactivity loss of filling material [291]. Thus, the transport, storage, and cost of the raw materials are the potential impediments. Besides, long-term activity, persistence, and dispersion of ZVI-based materials, the stability and mobility of the treated contaminants both entail the advanced, easy-synthesis, and low-cost ZVI-based materials [292-294].

1.1.5. Barriers in Market Penetration of ZVI-Based Materials in Removing Cr (VI)

From the acquisition of raw material, the preparation and performance evaluation

of ZVI-based materials from laboratory-scale to commercial applications, the barriers in market penetration are remained mainly attributed to the technology challenges, toxicity assessment to ecosystems, and the cost. The performance of ZVI-based materials in field trials or full-scale applications is rarely documented excluding nZVI. A pilot-scale in-situ remediation test was conducted with commercially available nZVI at Kortan in Hradek nad Nisou. The findings depicted that the concentration of Cr(VI) and total chromium in groundwater were substantially decreased after injecting nZVI with no observed effect on groundwater properties [295]. While, a lot of laboratory-based data has supported that template-supported nZVI or modified nZVI could prevent the agglomeration of the nZVI particles and impair non-target reactions [296, 297]. However, the longevity, reactivity, and removal mechanism of ZVI-based materials for Cr(VI) removal in field remediation are still unclear and act as an obstacle to the market penetration of this technology. The unintentional migration of nZVI through the soil, water, and air can threaten the ecosystem, especially for plant cells, animal cells, and microorganism cells [298, 299]. Thus, the toxicological effects of nZVI on organisms should be addressed in future research [300, 301]. In the commercialized application cases of ZVI, some companies prepared ZVI suspension with organic additives and dispersants to promote diffusion and delivery of ZVI. However, more organic additives are needed in terms of nZVI for the higher surface area and smaller particle size [288]. There would be more regulation considerations on the organic additives and dispersants to the ecosystem. Due to the presence of aggregation of nZVI in the subsurface environment, the nZVI has shown inferior migration than surface-modified nZVI, It was found that the migration of nZVI could be enhanced significantly after coated with starch and polyacrylic acid [302]. However, the potential environmental risks of ZVI-based materials are still unknown. Hence strategies to balance the potential environmental risks and expected environmental interests of ZVI-based materials would be required in clarifying the migration and toxicological impacts at specific sites. Further, as can be seen in Table 1-4, the demand amount of ZVI for a project was so high. Given price was \$0.55-15/lbs for ZVI from 325 μm to below 1 μm. It's a comparative high

expenditure for the ZVI during the remediation project. Compared to ZVI produced directly from the smelter, the ZVI derived from scrap iron and recycled material could lower the expenses remarkably. Regarding the sparing information about the actual cost for producing ZVI-based materials like sulfur-ZVI, Cu-ZVI, AC-ZVI, it's urgent to evaluate the cost for the synthesis of ZVI-based materials with scrap iron.

Table 1-4 ZVI remediation cases and the consumption (https://hepure.com/product-list/case-studies/)

Site background	Contaminant	Mode of application	In-situ or ex-situ	Dosage
Vadose zone soils beneath a large manufacturing facility	Cr(VI)	Hydraulic injection	In-situ	64,000 lbs
The facility had operated for 50 years as a machine shop where parts were degreased by a variety of solvents	PCE[a], TCE	PRB and injection	In-situ	154,000 lbs
Former Dry Cleaner	PCE	Injection	In-situ	401,310 lbs
Located in North Central Ohio	PCE, TCE, and VC[b]	Injection	In-situ	145,000 lbs

[a] Tetrachloroethene

[b] Vinyl Chloride

1.1.6. Conclusions

Altogether, the ZVI-based materials have been well-recognized and comprehensively employed for pollutants sequestration. This review has discussed four conventional ZVI-based materials (ZVI-AC/biochar, ZVI-sulfur, ZVI-magnetite, and bimetal of ZVI), two prevailing preparation methods (liquid reduction method and mechanical ball milling procedure), and their applications on Cr(VI) removal. The removal mechanisms have mainly involved the reduction, adsorption, and co-precipitation. Besides, the developed performance of ZVI-based materials regarding

the pristine ZVI could be attributed to the galvanic cell effect for ZVI-AC/biochar and bimetals of ZVI, and the regeneration of ferrous ions for sulfur-ZVI and magnetite-ZVI. Especially, the electron selectivity of ZVI to Cr(VI) was substantially controlled by the DO and pH of the solution. One of the most significant findings of this review is that the transfer of electrons from ZVI to Cr(VI) was appreciably dominated by five pathways. Briefly, the acidic/low oxygen condition facilitated the removal capacity of ZVI by generating more reductants, and the removal efficiency of ZVI on Cr(VI) was suppressed under acidic/oxygen-rich conditions due to the over-exhaustion of iron by oxygen, conversely. On the other hand, acidic/anaerobic conditions promoted the Cr(VI) removal through accelerating ZVI hydrogen-evolution erosion, and the erosion product aqueous ferrous ions were an effective reducing agent. The Cr(VI) removal rate was deteriorated under alkaline/aerobic conditions due to the more susceptible oxidation of Fe^{2+} by oxygen under alkaline conditions compared to acid conditions. The last pathway of DO and pH on iron capability under alkaline/anaerobic was that the produced Fe^{2+} contributed to the reduction of Cr(VI), which improved the removal efficiency of Cr(VI). The insights gained from this study may assist in groundwater remediation through PRB. Limited PRB field applications overlooked to consider the distribution of Cr(VI) concentration and flow velocity gradient in groundwater, which could help in optimizing the PRB dimension and avoid the uneven loss of ZVI media. More information on technology challenges, potential ecosystem risk, and cost of ZVI-based materials would help us to establish a greater degree of accuracy on the commercialization of this technology. The following are the key suggestions for future applications of ZVI-based materials:

- The selection of suitable ZVI-based materials is needed to reduce the unintentional consumption of ZVI by O_2, water, or other untargeted pollutants
- The solution chemistry of contaminated sites should be vigilantly evaluated because the utilization efficiency and selectivity to the aimed contaminants of ZVI in ZVI-based materials is greatly affected by pH and DO
- The large-scale and low-cost production of ZVI-based materials is necessary.

Although many ZVI-based materials have shown superior performance in the laboratory-scale or pilot stage, the practical performance is rarely available, like the PRB of ZVI-based materials

- Migration and toxicology of ZVI-based materials in the aquatic environment or soil are the potential ecological risk, thus the treated sites with ZVI-based materials would require long-term monitoring, and the used ZVI-based materials should be disposed of safely.

Chapter II. **Highly surface activated carbon to remove Cr(VI) from aqueous solution with adsorbent recycling**

2.1. Introduction

Chromium is a highly toxic contaminant in the effluents of electroplating and tanning factories, threatening the health of humans by bioaccumulation in the food chain [447]. Cr(VI) and Cr(III) are the two main chromium species. Cr(VI) shows a higher solubility, mobility, and toxicity as compared to Cr(III) [448]. There are not sparingly soluble Cr(VI) compounds, but in the case of Cr(III), Cr_2O_3 is a compound that has a very low solubility. Therefore to remove Cr(VI), it is a common practice to reduce soluble anion Cr(VI) to Cr(III) followed by precipitation. Conventional reducing agents for Cr(VI) are sulfur compounds and iron salts [447], which are effective in acidic conditions. Under these conditions, the predominant Cr(VI) species are $HCrO_4^-$ [449]. Salts with the sulfoxy species SO_3^{2-}, $S_2O_5^{2-}$ as well as $SO_2(g)$ are the most common reducing agents and rapidly reduce Cr(VI) at pH 2.5 [450, 451]. Fe^{2+} ions also reduce Cr(VI) at a high rate at low pH [452]. Under acidic conditions, Cr^{3+} ions are predominant, and aqueous solution pH should be increased with lime or base compounds to precipitate them as $Cr(OH)_3(s)$. The optimum removal conditions for Cr(VI) and Cr(III) are different from each other. $Cr(OH)_3(s)$ precipitates as ultrafine particles with low flocculation, settling, and filtration rates. As a result, the generated residue is a sludge with high moisture content and is difficult to dispose of as a green discharge. Other techniques have been proposed to remove Cr(VI) from aqueous solutions such as electrodialysis followed by precipitation and electroreduction [453-456], ion exchange [457], bioremediation [457] and modified zero-valent iron (ZVI) and zeolite materials [458, 459]. These techniques have the disadvantage of being of high energy consumption and high cost to produce the synthetic adsorbents.

AC has aroused attention for the removal of heavy metals because of its low cost and easy handling [460, 461]. AC presents a high specific surface area and surface functional groups and electron donors to convert Cr(VI) to Cr(III) [462-466]. It has been

found that removal of Cr(VI) is effective at acid conditions in the range of pH 2-4 [27, 37, 467]. At low pH, the AC surface functional groups are protonated, present a high reduction performance [231] and Cr(VI) reduces to Cr(III) and precipitates as Cr_2O_3(s) [468-470]. The high performance of AC for Cr(VI) reduction at low pH is similar to that shown by protonated *Ecklonia* biomass, which was 3.7 times higher than $FeSO_4 \cdot 7H_2O$ [471].

Most waters and soils contaminated with Cr(VI) possess a pH higher than 3.0 so their pH needs to be lowered to about 3 to remove the Cr(VI) according to these studies [472, 473]. Once the adsorption step is completed, the pH then has to be raised to around neutral values to reuse the water and soil. These two steps of pH adjustments could be avoided if the Cr(VI) removal were carried out at near-neutral pH. Under these conditions Cr(VI) is predominantly as CrO_4^{2-} and Cr(III) as $Cr(OH)_3$(s). After an extensive literature survey, we found that Cr(VI) removal from water at near-neutral pH has not been investigated in detail. Neither has been studied the Cr(VI) desorption from the AC and the AC recycling.

The main aim of this study was to establish the most suitable conditions for the removal of Cr(VI) with AC at near-neutral pH using an AC with a high density of functional groups to enhance the Cr(VI) adsorption and regenerating the AC for its recycling to the adsorption step. It is worth mentioning that this the first work facing these two aspects for the processing of waters contaminated with Cr(VI). Batch Cr(VI) adsorption tests were carried out at pH 6 and 7 with fresh and regenerated AC. The functional groups on the AC were characterized by electrokinetics and surface titration while the Cr species on the AC were identified by SEM (scanning electron microscopy) coupled to an EDX (energy-dispersive X-ray spectroscopy). AC with the high density of functional groups was prepared by high-intensity ball milling [315, 474].

2.2. Materials and methods

2.2.1. Adsorbents and chemicals

Granular coconut shell AC was purchased from Calgon Company. Its chemical composition was 97% C and 3% inorganic residues [469]. The HAC was prepared by ball

milling -20 μm size particles of AC for 60 min, using a planetary mono mill (Pulverisette 6, Fritsch, Germany) with steel balls of 5 mm in size as the grinding media. 10 g AC was mixed with the steel balls and milled at a speed of 300 rpm. This milled product is referred to highly activated carbon (HAC) throughout this manuscript. Its D_{80} (particle size of cumulative undersize at 80%) size of the HAC was found to be 4μm, the specific surface area was 928.5 m^2/g, and the mean pore size was 15.3 Å. The HAC was dried at 60 ^oC for 24 hours, then kept in a plastic flask in a glass desiccator. Analytical grade potassium dichromate ($K_2Cr_2O_7$) was the source of Cr(VI) and acquired from J.T.Baker. A stock solution with a concentration of 1,000 mg/L Cr(VI) was prepared for all the adsorption tests. All aqueous solutions were prepared with deionized water of 18.2 Ω, which was obtained by passing distilled water through a Barnstead E-pure II Water Purification Systems, Thermo Scientific, USA. 1.0 mol/L aqueous solutions of both sulfuric acid and sodium hydroxide were used to adjust the pH in the adsorption tests. All other inorganic chemical reagents such as H_2SO_4, H_3PO_4, NaOH, and $NaHCO_3$ were of analytical grade.

2.2.2. Adsorbent characterization

Adsorbed chromium species on HAC were determined through SEM coupled to an EDAX. The surface functional carboxyl and hydroxyl (phenolic, hydroxyl, and lactols) groups of the AC and HAC were quantified by Boehm's titration method [475]. Briefly, the method is as follows: stir 200 mg AC in 100mL deionized water with the desired $NaHCO_3$ and NaOH concentration for 20 hours, take a 50 mL aliquot and titrate it with a normalized HCl aqueous solution. The content of carboxyl and hydroxyl groups was determined from the loss of $NaHCO_3$ and the loss difference of NaOH and $NaHCO_3$, respectively.

A Zeta Probe equipment (Colloidal Dynamics, USA) was employed to determine the zeta potential of AC and HAC. For these measurements, a 3 g sample was stirred ultrasonically in 100 mL with a 0.01mol/L NaCl concentration at 150 rpm for 5 min. For the zeta potential measurements, 0.1 mol/L of both HCl and NaOH aqueous

solutions titrated automatically the carbon suspension for pH adjustment throughout the zeta potential quantification. All these measurements were performed at 22°C. The equipment uses the electrokinetic sonic amplitude (ESA) to determine the zeta potential of particles in suspensions. Two electrodes with a high-frequency electric field are immersed in the suspension. For the moment, the particles oscillate back and forth with the electric field and most of the particle oscillations cancel one another out, but the oscillation does not take place near the electrodes, and a sound wave is generated from there. The sound wave would hit a transducer along the delay rod. Therefore, the transducer will produce a sinusoidal voltage signal by vibration. The generated amplitude value of the sinusoidal voltage signal equals the ESA number. The mathematic relation between ESA and dynamic mobility (μ_d) is given by Eq (2-1) [476, 477].

$$\mathrm{ESA} = \mathrm{A}(\omega)\varphi\frac{\Delta\rho}{\rho}Zu_d \tag{2-1}$$

where A(ω) is the instrument calibration factor, which can be determined by calibration with potassium silico tungstate solution (KSiW), φ is the particle volume fraction (3% in our study), Δρ is the density difference between particle (1.91 g/cm^3) and solvent (1.00 g/cm^3), ρ is the solvent density and Z is a factor related to the acoustic impedance of suspension and delay rod of the instrument. Finally, u_d was converted to zeta potential (ζ) by Henry's equation, represents as Eq (2-2) [478]:

$$u_d = \left(\frac{2\varepsilon\zeta}{3\eta}\right)f(\kappa a) \tag{2-2}$$

where ε is the dielectric constant, η is the water viscosity, f(κa) is Henry's factor. A simple value for f(κa) is 1.5, referred to the modified Smoluchowski equation [479]

The specific surface area and pore size of HAC before and after Cr(VI) adsorption were determined by gas adsorption measurement using an Autosorb-1, Quantachrome instrument. A desired amount of sample was heated and degassed at 80 °C before analysis, then nitrogen adsorption and desorption were conducted at 77.3 K liquid nitrogen. The multipoint BET, BJH methods were used to calculate the specific surface area and pore size, respectively.

Raman spectra (DXR, Thermo scientific, USA) were utilized to obtain the detailed carbon structure change caused by ball milling and XPS (X-ray photoelectron spectroscopy) was used to determine the C, N, S, and O elements content.

2.2.3. Cr(VI) uptake experiments

Adsorption kinetics studies were performed with 5g adsorbent and 100 ml, 1000 mg/L Cr(VI) at pH 6 and 7. A 20 µL aliquot was withdrawn from the aqueous solution at various time intervals such as 0.25, 0.5, 1, 3, 5, 7, 9, 12, 15, 30, 60, 120 mins. The aliquot was analyzed for Cr(VI) and total Cr. Adsorption isotherms were built within a Cr(VI) concentration range of 800 to 2000 mg/L at 295, 308, and 323 K by contacting the adsorbent with the Cr(VI) for 24 h. Before the addition of Cr(VI), the AC and HAC were pre-treated for the equilibrium of their surface groups with the aqueous solution as follows: 5 g adsorbent was mixed with 100 mL deionized water, and the pH was stabilized at 6 and 7 until the pH did not change, which occurred at about 30 mins. Then, potassium dichromate was introduced to the suspensions at the desired Cr(VI) concentration.

The HAC suspension was stirred in a 250 mL Erlenmeyer flask using a Thermo scientific magnetic stirrer at 400 rpm at 22 ^{o}C. An aliquot of 100 µL was withdrawn from the aqueous suspension and centrifuged at 8,000 rpm for 10 min using an Allegra^{TM} 21 Centrifuge (Beckman coulter, USA). The supernatant was analyzed for total Cr and Cr(VI). Total Cr was determined through atomic absorption spectrophotometry, while the Cr(VI) by a colorimetric method using a UV/Vis spectrophotometer (Thermo Scientific, USA. with a light path of 1 cm) at 540 nm. 1,5–diphenylcarbazide was used as an indicator [480]. The concentration of Cr(III) was determined by the difference between total Cr and Cr (VI). Unless otherwise stated, all the adsorption experiments were performed with a blank control at 22^{o}C.

2.2.4 Cr desorption from HAC after treatment with Cr(VI)

Cr (VI) desorption from the HAC and HAC surface regeneration was carried out by acid and alkali elution experiments. First, HAC and pristine AC were repeatedly contacted (four times) with a 1,000 mg/L Cr(VI) aqueous solution to obtain a Cr-loaded material. The Cr-loaded HAC (0.5g) and Cr-loaded AC (0.5g) were then treated with 0.2 mol/L H_2SO_4 (50 ml) and 0.1 mol/L NaOH (50 ml) aqueous solutions. The amount of desorbed chromium (mg/g) after elution was determined as follows;

$$q = \frac{C_t V}{m} \quad (2\text{-}3)$$

where q (mg/g) is the chromium content desorbed from the carbon materials, C_t (mg/L) is the chromium concentration in the eluted solution at time t, V (L) is the volume of the elution solution and m (g) is the mass of the material.

2.2.5 Regeneration and reusability of HAC

Consecutive adsorption tests were conducted to investigate the reusability of HAC on Cr(VI) (1000mg/L) adsorption. The HAC was contacted with an H_2SO_4 solution of 0.1 mol/L for 24 hours stirring the suspension at 400 rpm in a magnetic stirrer to regenerate the surface of the HAC treated with Cr(VI) solution [481]. This regenerated material was then used in the next Cr(VI) adsorption test.

2.3. Results and discussions

2.3.1. Effect of ball milling on Cr(VI) sequestration

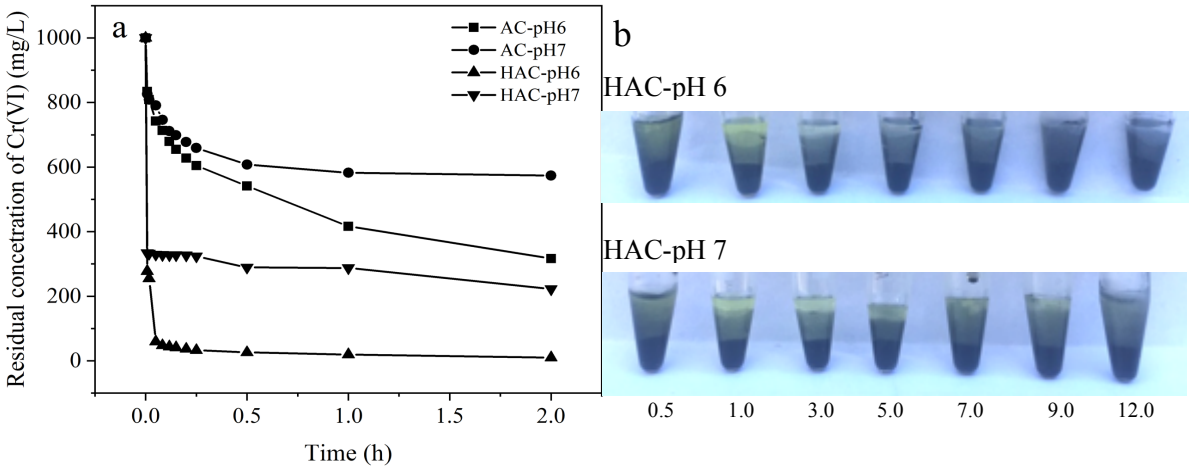

Figure. 2-1 (a) The depletion curve of Cr(VI) by AC and HAC under pH 6 and 7 as

time (AC average size is 20μm, HAC average size is 4μm, dose 5g/100ml, 1000mg/L Cr(VI), RPM=350, 295K); (b) The aqueous solution color change as time of Cr(VI) removal by HAC.

Fig. 2-1 (a) depicts the depletion of Cr(VI) concentration as a function of time at pH 6 and 7. It is seen that for both pHs, the Cr(VI) concentration depletion was very fast in the first 0.25 hour, being this depletion larger at pH 6. The Cr(VI) removal by HAC was 99.0% and 77.8% at pH 6 and 7 after 2 hours, respectively. These Cr(VI) removals were larger than those on pristine AC (68.3% at pH 6 and 42.7% at pH 7). Thus, a significant increase in Cr(VI) removal was achieved with the HAC. The figure also shows photos of the Cr(VI) aqueous solutions at various times at the two pH values. The increase in Cr(VI) adsorption can be associated with the increase of the functional groups on the AC. In Fig. 2-1 (b), it is noted that the color of the Cr(VI) aqueous solution became more crystal clear at pH 6 than at pH 7, clearly indicating that more Cr(VI) was removed at pH 6.

2.3.2 Characterization of materials

2.3.2.1 Surface and texture chemistry of materials

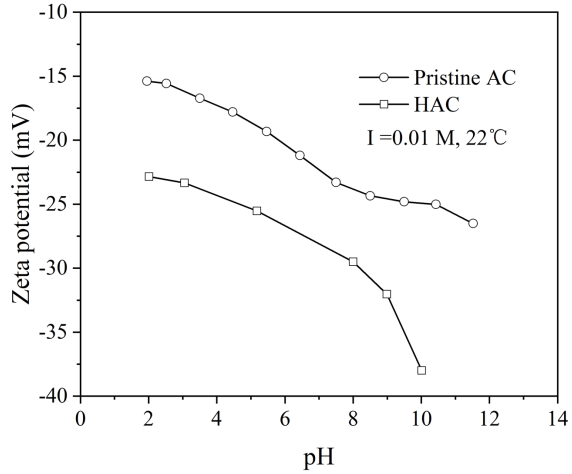

Figure. 2-2 Zeta Potential of AC (20μm) and HAC (4μm) as a function of pH

Fig.2-2 shows the zeta potential of pristine AC and HAC as a function of pH. It is seen that the zeta potential decreased negatively as the pH increased, as reported

elsewhere [482, 483]. The negative zeta potential of AC and HAC is due to the dissociation of their acidic functional groups [484] and Chingombe et al. (2005) have reported that the zeta potential of AC becomes more negative as the acid functional groups increased. As noted in Fig. 2-2, the zeta potential of HAC is more negative than that of AC, indicating that the ball milling promoted the formation of acid functional groups of the carboxylic type. This was confirmed by determining the surface density of the functional groups before and after milling. Table 1 presents the surface density of the total acidic and alkaline functional group before and after milling, as well as after adsorption of Cr(VI). It is noted that the total acidic group of the AC increased from 1.31 mmol/g to 1.84 mmol/g after grinding, due mainly to the increase of COOH groups. Our results are consistent with those of Lyu et al. (2018) who have reported that the total acidic groups in biochar increased from 0.3 mmol/g to 1.35 mmol/g after high intensity grinding of the biochar [485]. Recent studies proved that more oxygen/hydrogen functional groups were introduced into activated carbon during the ball milling and increased the hydrophilicity of activated carbon [13, 16]. As noted in Table 2-1, after Cr(VI) adsorption no carboxylic groups were detected on the HAC. This can be accounted for by the shielding of these groups by adsorbed Cr(VI) as explained below. Therefore, the COOH groups played a vital role in Cr(VI) adsorption. The increase in hydroxyl surface density after adsorption is due to $Cr(OH)_3$, which is formed from the reduction of Cr(VI).

Table 2-1 The surface chemical properties before and after ball milling AC and HAC treated with Cr(VI)

Sample	Total acidic group (mmol/g)	Carboxyl (mmol/g) -COOH	Phenolic, hydroxyl, lactols (mmol/g) -OH
Pristine AC	1.31	0.31	1.00
AC after milling HAC	1.84	0.97	0.87
HAC after Cr(VI) adsorption	1.94	ND	1.94

ND is no detectable

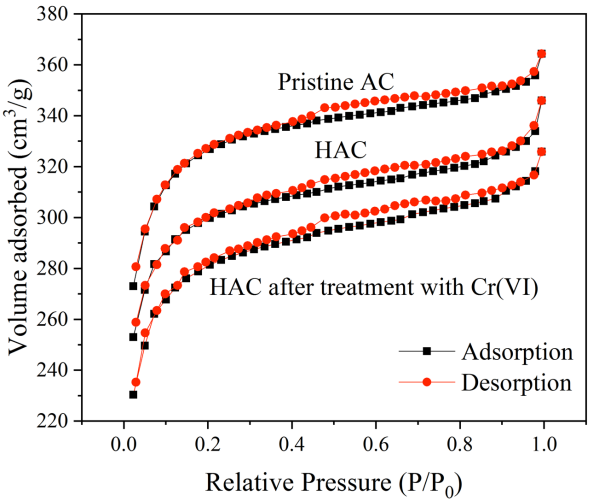

Figure. 2-3 N_2 adsorption-desorption isotherms (BET) of pristine AC, HAC and HAC treated with Cr(VI).

The N_2 adsorption and desorption isotherms and pore size of pristine AC, HAC, and after adsorption are shown in Fig. 2-3. Referring to the classification of physisorption isotherms [486], the N_2 adsorption and desorption curves of the three materials fitted well with the type IV adsorption isotherm (IUPAC classification). The hysteresis loop in Fig.2-3 ascribed to H4 type means a narrow slit-like pore structure, commonly seen in micropore activated carbon materials [487]. The higher surface area of HAC can be associated with its smaller particle size in comparison to that of AC. After adsorption of Cr(VI), the surface area of HAC decreased and the pore size increased, which is due to the filling of adsorbed Cr in the pores. Figs. 2-4 and 2-5 show SEM photomicrographs of Cr-loaded HAC. As noted, there is chromium on the surface and inside of the HAC, being the content of chromium on the surface much higher than that inside the particle. A similar texture to that seen in Fig. 2-5 has been reported by Wang et al. (2020). They reported the formation of an eskolaite (Cr_2O_3) layer on the AC surface, which lowers the Cr(VI) adsorption capacity of AC and the diffusion of Cr(VI) to the interior of the AC particle.

Table 2-2 Pore structural parameter of AC, HAC, and HAC after Cr(VI) adsorption

Materials	Average particle size (μm)	Specific surface area (m^2/g) (BET)	Pore size (Å) (BJH)
Pristine AC	20	846	19.0
HAC	4	929	15.3
HAC after Cr(VI) adsorption	4	876	18.5

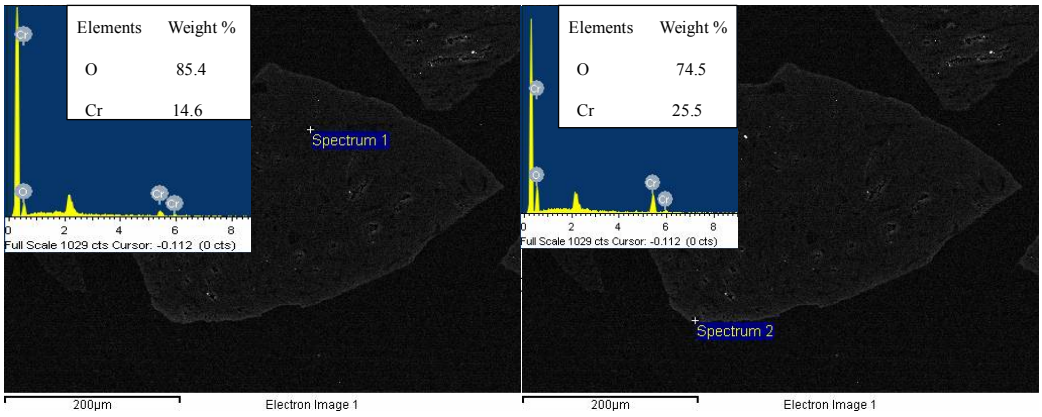

Figure. 2-4 SEM photomicrograph and quantitative analysis EDX pattern after HAC adsorption at pH 7.

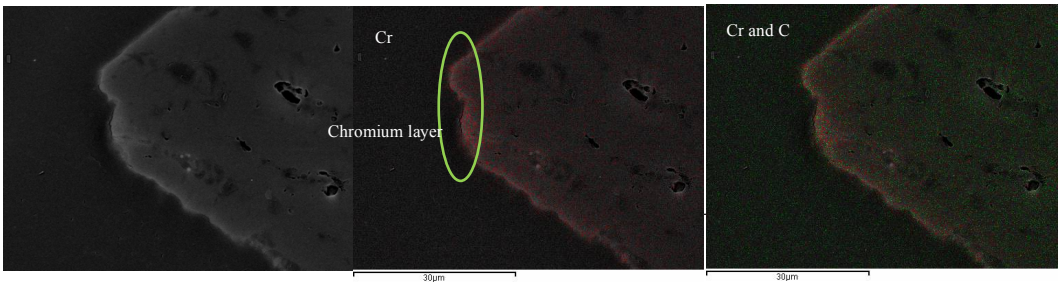

Figure. 2-5 SEM figure and SEM-EDX elements mapping of HAC after adsorption at pH 7.

As can be seen in Figs 2-4 and 2-5, chromium was detected on the surface and inside of the HAC particle, being the content of chromium on the surface much higher than that inside the particle. Table 2-2 compares the summary statistics of surface area and pore size analysis results, it noticeable from this table that the chromium in the HAC lowered the specific surface area and mean pore size of the HAC from 929 m^2/g

to 876 m^2/g and 15.3 Å to 18.5 Å, respectively. A similar texture to that seen in Fig. 2-5 has been reported by Wang et al. (2020) in Cr-loaded AC particles after adsorption at pH 3 [468]. They reported the formation of an eskolaite (Cr_2O_3) layer on the AC surface, which lowers the Cr(VI) adsorption capacity of AC and the diffusion of Cr(VI) to the interior of the AC particle. Besides, the increased BET surface area of HAC generated by ball milling may be explained by the decreased particle size and the deformation of the carbon structure.

2.3.2.2 Raman spectra investigation

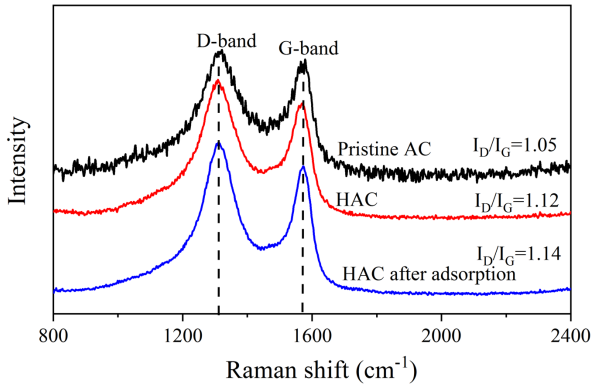

Figure. 2-6 Raman spectra of pristine AC, HAC and HAC after adsorption of Cr(VI).

Fig. 2-6 shows the Raman spectra of AC, HAC, and HAC after Cr(VI) adsorption. the D-band (1320cm^{-1}) and G-band (1563cm^{-1}) in the spectra reveal the degree of lattice distortion of any carbon material, The D-band represents the stretch vibration of sp^3 hybridized carbon, while the G-band is related to the sp^2 graphited carbon [488]. It has been reported that the ratio of the intensity of D-band versus G-band (I_D/I_G) indicates the level of graphitization or structural order of carbon materials [489]. As noted in Fig 2-6, the I_D/I_G of HAC increased from 1.05 for pristine AC to 1.12 and further increased to 1.14 after adsorption of Cr(VI). The increase of I_D/I_G for HAC revealed that ball milling enhanced the formation of sp^3 defects in the carbon structure. Moreover, the increase of sp^3-bonding hybridized carbon atoms of HAC after Cr(VI adsorption may due to the reduction of surface oxygen-containing functional groups [490]. Various studies have demonstrated that the reduction of surface oxygen-containing functional groups caused the formation of amorphous carbon structure [491, 492]. The increase of surface

functional groups for HAC by ball milling seems to be contradictory with the increase of disorder of structural carbon. This inconsistency may be due to the relatively more produced hybridized carbon atoms by ball milling compare to the increase of oxygen-containing groups.

The content of C, O, N, and S in HAC and HAC after Cr(VI) adsorption was determined through XPS and the results are presented in Table 2-3. It is seen that the C content decreased after Cr(VI) adsorption and the O element increased. The decrease of carbon content can be related to the decline of C-containing surface functional groups, coupled to the reduction of Cr(VI) to Cr(III). The increase of O content can be associated with the chromium oxide resulting from the Cr(VI) reduction, proving that a chromium species containing oxygen formed from the Cr(VI) reduction.

Table 2-3 The elements analysis of HAC and treated HAC with Cr(VI)

	C	N	O	S
HAC (%)	91.24	0.93	6.86	0.97
Treated HAC (%)	84.58	0.50	13.01	1.91

2.3.3. Adsorption kinetic

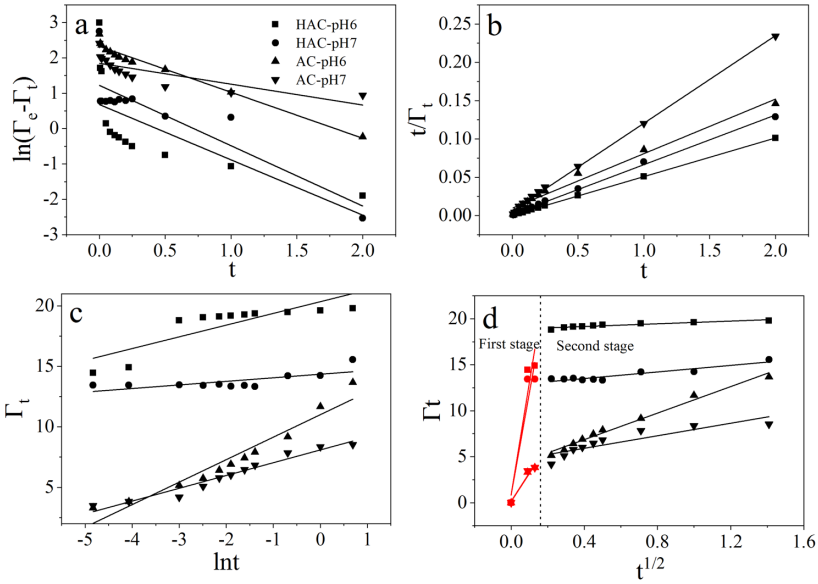

Figure. 2-7 The linear fit for experimental date of Cr(VI) removal by HAC and AC under pH 6 and 7, (a) Pseudo-first order, (b)Pseudo-second order, (c) Elovich, (d) Interparticle diffusion

To investigate the adsorption kinetics of aqueous Cr(VI) adsorption on pristine AC and HAC, and recognize the divergence of the rate constant before and after ball milling. The kinetics models of Pseudo-first order, Pseudo-second order, interparticle diffusion, and Elovich were employed and the general forms as Eqs (2-4)-(2-7) [493, 494].

Pesudo-first order model

$$\ln(\Gamma_e - \Gamma_t) = \ln\Gamma_e - k_1 t \quad (2\text{-}4)$$

Pseudo-second order model

$$\frac{t}{\Gamma_t} = \frac{t}{\Gamma_e} + \frac{1}{k_2 \Gamma_e^2} \quad (2\text{-}5)$$

Weber-Morris Interparticle diffusion model

$$\Gamma t = k_3 t^{1/2} + I \quad (2\text{-}6)$$

Elovich model

$$\Gamma_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (2\text{-}7)$$

where Γe(mg/g) is the adsorption density at equilibrium, Γt(mg/g) is adsorption density at time t, k_1 (h^{-1}) is the rate constant of Pesudo-first order model, k_2 (mg/g·h) is the rate constant of Pesudo-second order, k_3 and I are the constants of interparticle diffusion, α (mg g^{-1} h^{-1}) and β (g mg^{-1}) are the initial sorption rate of adsorbate and desorption constant, respectively.

As shown in Figs. 2-7, the Cr(VI) adsorption data were linearly fitted with adsorption kinetic models, the detailed parameters for models were presented in Table 4. The Cr(VI) removal is described well with Pseudo-second order kinetic model for HAC and AC under pH 6 and pH 7 with higher correlation coefficients (r^2), suggesting that the interaction between the Cr(VI) and the functional groups of the HAC and AC is of the chemical type. As described in Table 2-4, the rate constant of k_2 at pH 6 was nearly 3 times greater than that at pH 7 for HAC, and the rate constant for HAC under pH 6 and 7 both increased after ball milling compared to the pristine AC. Indicating that the adsorption rate was highly favorable with the hydrogen ion strength and the developed Cr(VI) removal capacity on HAC was associated with the quicker chemical reaction between Cr(VI) and surface functional groups. Besides, the chemical reaction

associated with the Cr(VI) adsorption was significantly related to the proton concentration, in agreement with studies reported previously [27, 471, 495-497].

Table 2-4 The adsorption kinetic model parameters for Cr(VI) removal by AC and HAC under pH 6 and 7

	HAC		Pristine AC	
Models	pH6	pH7	pH6	pH7
Pseudo-first order				
Γe (mg/g)	1.97	3.39	10.28	6.36
k_1 (h^{-1})	1.56	1.71	1.30	0.59
r^2	0.461	0.746	0.972	0.627
Pseudo-second order				
Γe (mg/g)	20	15.38	14.08	8.77
k_2 (mg/g·h)	8.39	2.88	0.53	2.23
r^2	1.000	0.998	0.983	0.999
Elovich				
α (mg g^{-1} h^{-1})	1.3×10^{9}	1.9×10^{21}	199.0	1946.5
β (g mg^{-1})	0.97	0.30	1.86	1.06
r^2	0.755	0.951	0.978	0.985
Interparticle diffusion				
k_{id1}	122.39	111.24	30.64	30.94
I_1	0.81	0.81	0.13	0.16
r_1^2	0.924	0.910	0.967	0.951
k_{id2}	0.73	1.78	7.20	3.40
I_2	18.86	12.79	3.98	4.55
r_2^2	0.880	0.892	0.986	0.799

The diffusion process of aqueous adsorbate into adsorbent can be elucidated by the Interparticle diffusion model. Briefly, the adsorbate ions transfer through bulk solution into the external surface of the adsorbent and then transfer into the internal surface followed by adsorption in the active sites of adsorbent [498]. As can be seen in Fig. 2-7 (d), the diffusion route of Cr(VI) into AC and HAC contains two steps. The first stage of adsorption dominants the removal rate of Cr(VI) by AC and HAC since the interparticle diffusion rates at the first stage (k_{id1}) for AC and HAC were both higher than that of the second stage (k_{id2}). The k_{id1} of HAC under pH 6 and 7 were nearly 4 times higher than that of AC, this finding has identified that the rate of Cr(VI) transfers from the bulk solution to the surface of AC was improved after ball milling pretreatment.

2.3.4 Adsorption isotherm

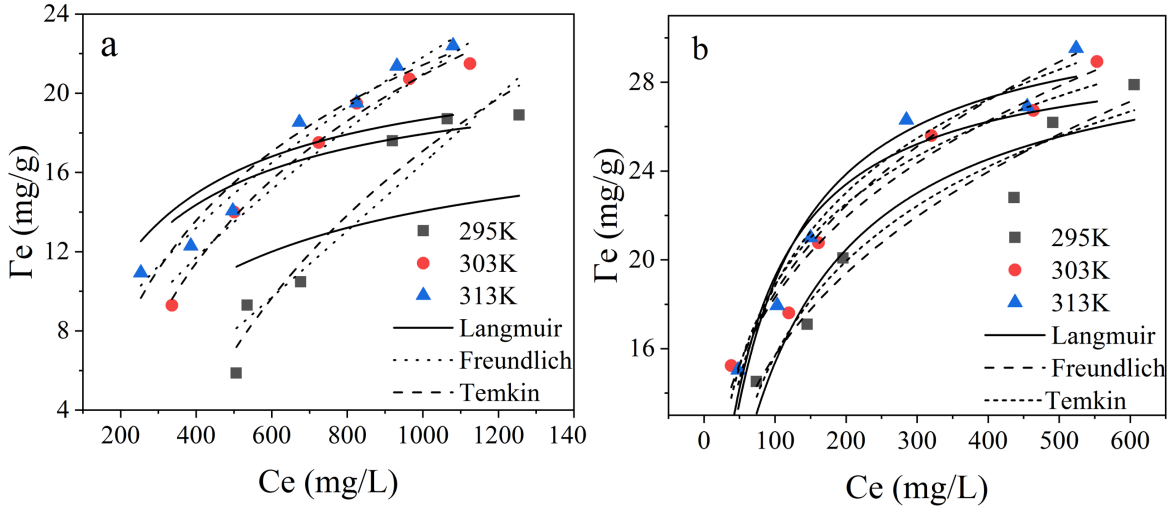

Figure. 2-8 Non-linear fit of adsorption isotherm models (a) AC (b) HAC (pH 7, 50g/L).

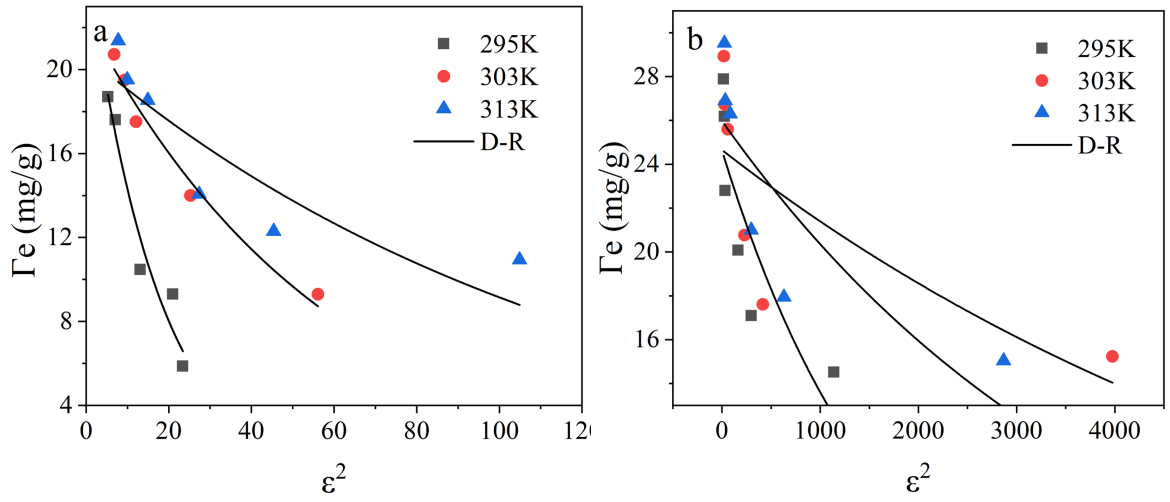

Figure. 2-9 Non-linear fit of D-R model for (a) AC and (b) HAC (pH 7, 50g/L).

Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin models were employed to delineate the adsorption behavior of Cr(VI) [499], the non-linear equations of those models were presented as follows;

Langmuir equation

$$\Gamma e = \frac{K_L \Gamma_0 C_e}{1+K_L C_e} \quad (2\text{-}8)$$

Freundlich equation

$$\Gamma e = K_F C_e^{1/n} \quad (2\text{-}9)$$

Temkin equation

$$\Gamma e = \frac{RT}{b_T} \ln (K_T C_e) \quad (2\text{-}10)$$

D-R equation

$$\Gamma e = \Gamma_{max} e^{-K_D \varepsilon^2} \quad \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (2\text{-}11)$$

where Γe (mg/g) is the equilibrium adsorption density, Γ_0 (mg/g) is the theoretical monolayer adsorption density, K_L (L/g) is the Langmuir constant, K_F is the Freundlich isotherm constant, Ce (mg/L) is equilibrium concentration, n is the Freundlich isotherm exponent, R (8.314 J/mol/K) is the universal gas constant, T (K) is the absolute temperature, b_T (J/mol) is the Temkin isotherm constant, K_T (L/g) is the Temkin isotherm equilibrium binding constant, Γmax (mg/g) is the theoretical saturation density, K_D ($mol^2\ kJ^{-2}$) is the D-R isotherm constant, ε is the Polanyi potential.

Figs. 2-7 and 2-8 were the non-linear fit of Langmuir, Freundlich, Temkin, and D-R isotherm models, the computed theoretical parameters of the models were provided in Table 2-5. The higher correlation coefficients of the Freundlich model fitted the experimental data satisfactorily and this observation could support the hypothesis that the adsorption of Cr(VI) on AC and HAC was multi-layer. The values of n for HAC were all over 2 while values of n for AC were all below 2, which indicated the adsorption was favorable for HAC under ambient temperature [500]. Table 2-6 listed the adsorption density comparison of different AC materials with this study.

Table 2-5 The parameters of adsorption isotherm models for HAC and AC

		AC			HAC		
Models		295	303	313K	295	303	313K
Langmuir	Γ_0 (mg/g)	18.9	21.5	22.4	31.6	31.7	32.6
	K_L (L/mg)	0.003	0.005	0.005	0.014	0.009	0.014
	r^2	0.438	0.600	0.704	0.919	0.851	0.947
Freundlich	K_F	0.002	0.158	0.441	3.843	5.523	5.179
	1/n	1.303	0.714	0.567	0.306	0.260	0.277
	r^2	0.942	0.982	0.973	0.962	0.970	0.971
Temkin	b_T (J/mol)	153.2	239.6	310.0	423.7	491.8	429.6
	K_T (L/g)	0.003	0.007	0.013	0.128	0.353	0.224
	r^2	0.904	0.997	0.945	0.949	0.941	0.971
D-R	Γmax (mg/g)	25.5	22.5	20.68	24.64	24.66	25.99
	K_D (mol^2 kJ^{-2})	0.058	0.017	0.008	5.9E-4	1.4E-4	2.4E-4
	r^2	0.950	0.977	0.793	0.706	0.545	0.697

Table 2-6 Comparison of Cr(VI) adsorption density onto various AC materials

Adsorbents	Adsorption density (mg/g)	pH	Refs
Commercial AC	20.0	7	[501]
Polysulfide rubber modified AC	8.9	4	[502]
Pomegranate husk AC	10.0	6	[503]
Chestnut oak shells AC	6.0	7	[504]
Tannic acid immobilized AC	0.5	7	[505]
Hazelnut shell AC	8.0	8	[506]
Granular AC	7.2	7	[507]
Fe-modified AC prepared from Trapa natans husk	2.5	7	[508]
Micron-scale iron modified AC	1.3	6	[106]
AC derived from seagrass	0	≥4	[509]
Ball milled AC	28.9	7	This study

2.3.5. Adsorption thermodynamic

The thermodynamic parameters enthalpy change (ΔH) and entropy change (ΔS) can be calculated by the function of $\ln K_C$ versus 1/T, the equation shown in Eq (2-12). Gibb's free energy change (ΔG) can be determined through the Van't Hoff equation (Eq (2-13)).

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2\text{-}12)$$

$$\Delta G = -RT\ln K_c \quad (2\text{-}13)$$

Where ΔH (kJ/mol) and ΔS (J/mol k) were established by the slope and intercept of Eq(12). The adsorption process is endothermic if the value of ΔH is positive, otherwise, it's exothermic. Equilibrium constant K_C equal to Γe/Ce [27] or the intercept of the plot of ln(Γe/Ce) versus Γe [510], the negative value of ΔG (kJ/mol) means the adsorption process prolongs spontaneously under ambient conditions.

The detailed values of ΔH, ΔS, and ΔG of Cr(VI) adsorption on HAC and AC are given in Table 2-7. The values of ΔG for HAC and AC were both negatives, signifying that the adsorption of Cr(VI) was spontaneous and the values ΔG of HAC under different temperatures were both higher than that of AC, which implied the spontaneity of adsorption was unfavorable energetically and more spontaneity for HAC after ball milling [511]. The value of ΔH was positive for HAC and AC indicated the Cr(VI) adsorption process was endothermic. Positive values of ΔS of HAC and AC related to the disorderliness of the system.

Table 2-7 The adsorption kinetic model parameters for Cr(VI) removal by AC and HAC under pH 6 and 7

Adsorbents	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol k)
	295	-11.80		
HAC	303	-12.12	0.001	0.04
	313	-12.52		
	295	-17.69		
AC	303	-18.17	0.01	0.06
	313	-18.77		

2.3.6 Cr(VI) removal mechanism

2.3.6.1 The pH-speciation of Cr(III) and Cr(VI)

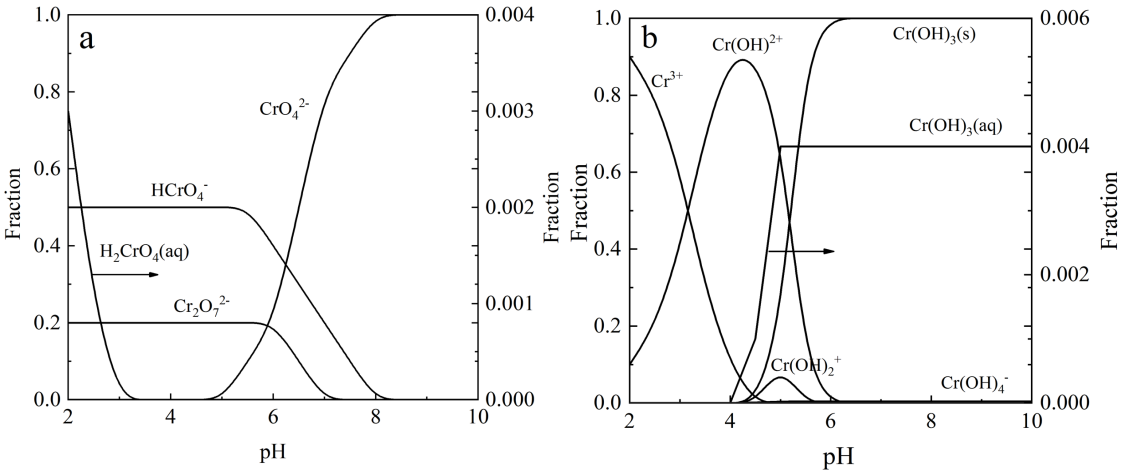

Figure. 2-10 The speciation diagram of (a) Cr(VI) and (b) Cr(III).

Fig. 2-10 is the pH-speciation diagram for 1000 mg/L Cr(VI) and Cr(III), which were built using equations (14)-(21). $HCrO_4^-$ and CrO_4^{2-} are predominant at pH 6, while CrO_4^{2-} predominates at pH 7. As shown in Figure 2-10 (b), $Cr(OH)_3$(s) is the predominant species both at pH 6 and pH 7. The aqueous solution chemistry equilibriums for Cr(VI) and Cr(III) species are shown in Eqs (2-14) to (2-21) [512-514], where k is the chemical reaction equilibrium constant [515].

$H_2CrO_4 = HCrO_4^- + H^+$ $\quad k = 10^{-0.43}$ (2-14)

$HCrO_4^- = CrO_4^{2-} + H^+$ $\quad k = 10^{-6.49}$ (2-15)

$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$ $\quad k = 10^{1.55}$ (2-16)

$Cr^{3+} + H_2O = Cr(OH)^{2+} + H^+$ $\quad k = 10^{-3.56}$ (2-17)

$Cr(OH)^{2+} + H_2O = Cr(OH)^+_2 + H^+$ $\quad k = 10^{-6.27}$ (2-18)

$Cr(OH)^+_2 + 2H_2O = Cr(OH)_3(aq) + H^+$ $\quad k = 10^{-2.61}$ (2-19)

$Cr(OH)_3(aq) + H_2O = Cr(OH)_4^- + H^+$ $\quad k = 10^{-10.33}$ (2-20)

$Cr(OH)_3(aq) = Cr(OH)_3(s)$ $\quad k = 10^{4.17}$ (2-21)

It is noteworthy to remark that most studies on Cr(VI) removal have been undertaken at acidic conditions where $HCrO_4^-$ and Cr^{3+} are the predominant species. Under these pH conditions, Cr_2O_3(s) has been reported to be the end chromium product

on AC [468-470]. Our work was carried out at pH 6 and 7. Under these pH conditions, $Cr(OH)_3(s)$ was the chromium product on the AC as discussed below.

2.3.6.2 Chromium species on HAC

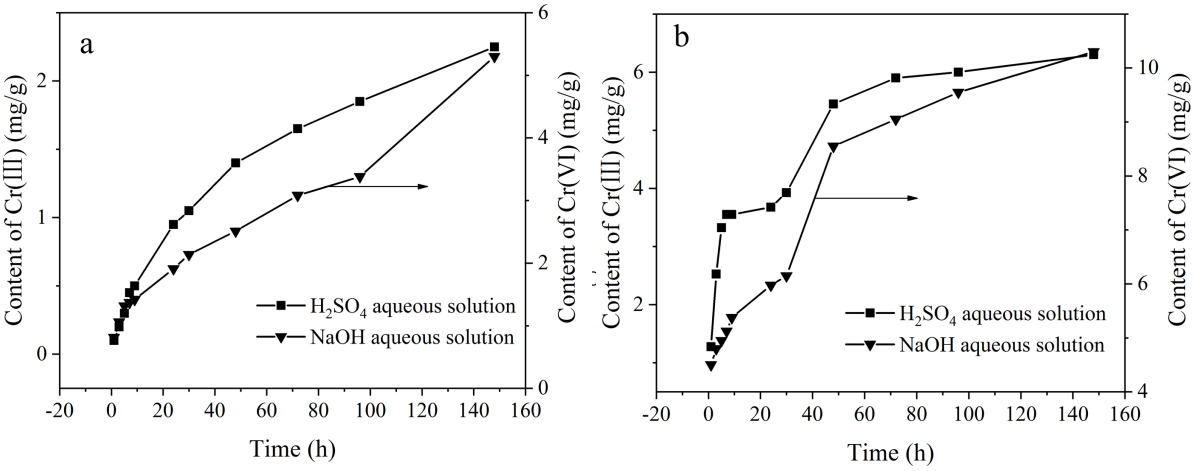

Figure. 2-11 The elution experiments with chromium-loaded virgin AC (a) and HAC (b) after adsorption at pH 7 (1.0 g/100ml treated pristine AC or HAC, 0.2 M H_2SO_4 and 0.1 M NaOH, 295K)

Fig. 2-11(a) and (b) show the amount of Cr(III) and Cr(VI) desorbed from AC and HAC, after treatment with Cr(VI) at pH 7, using a 0.2 M H_2SO_4 and 0.1 M NaOH aqueous solution. Firstly, it is noted that Cr(III) desorbed from the carbons at acidic pH conditions, while Cr(VI) desorbed at basic pH. The Cr(III) in the eluants at acidic conditions likely results from the dissolution of $Cr(OH)_3$, leading to say that this is the Cr(III) species which formed from Cr(VI) adsorption. Cr(VI) in the eluants at basic conditions suggests that Cr(VI) co-adsorbed with the $Cr(OH)_3(s)$ as CrO_4^{2-}. At basic pH, OH^- ions deprotonated the surface COOH groups, which is turned into the electrically negative COO- group. As a result, the adsorbed CrO_4^{2-} on the COOH is repelled and migrated to the aqueous solution. Desorbed Cr(VI) was 10.3 mg/g from HAC, much greater than the Cr(VI) desorbed from AC, which was 5.3 mg/g. Dissolved Cr^{3+} from HAC reached 6.3 mg/g, almost 3 times greater than the Cr^{3+} desorbed from AC. The much greater amount of chromium desorbed from the HAC in comparison to

that desorbed from AC confirmed that high-intensity ball milling improved the adsorption performance of AC. More functional groups, especially carboxyl, were created on the AC surface, which in agreement with the work reported by [17, 485]

The chromium elution under acidic and alkaline solution can be stated as Eqs (2-22) and (2-23), respectively.

$$HAC\cdots Cr(OH)_3(s) + 3H^+ \rightarrow HAC + Cr^{3+} + 3H_2O \quad (2\text{-}22)$$

$$HAC\text{-}COOH\cdot\cdot CrO_4^{2-} + OH^- \rightarrow CrO_4^{2-} + HAC\text{-}COO^- + H_2O \quad (2\text{-}23)$$

2.3.6.3 Proposal on chromium removal mechanism

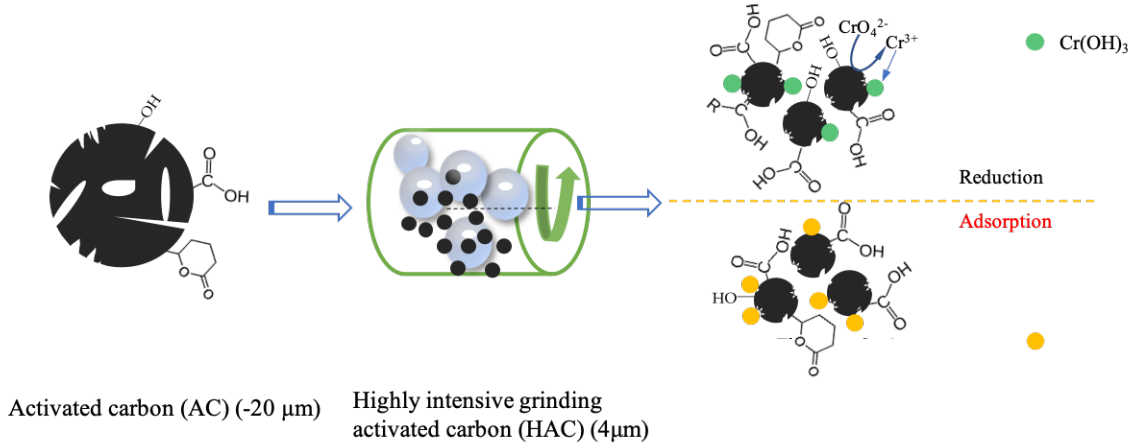

Figure. 2-12 Schematic of Cr(VI) removal by HAC induced by ball milling.

The tests on chromium elution from the Cr-loaded HAC showed that Cr(III) as $Cr(OH)_3(s)$ and Cr(VI) as CrO_4^{2-} were on the surface of HAC. The $Cr(OH)_3(s)$ formed a layer on the HAC particle, as seen in Figs 2-4 and 2-5. This $Cr(OH)_3(s)$ resulted from the reduction of adsorbed Cr(VI) to Cr(III). According to Fig 2-10(b), $Cr(OH)_3(s)$ is the stable Cr(III) species at pH 6 and 7. The reduction of Cr(VI) to Cr(III) has been proposed to be due to π-electron in activated-carbon-basal planes [516-518]. The reduction of Cr(VI) to Cr(III) and the surface precipitation of $Cr(OH)_3$ can be expressed as follows:

$$CrO_4^{2-} + 8H^+ + 3e^- = Cr^{3+}(aq) + 4H_2O \quad (2\text{-}24)$$

$$Cr^{3+} + 3H_2O = Cr(OH)_3(s) + 3H^+ \quad (2\text{-}25)$$

Adsorption of Cr(VI) may proceed through hydrogen bonding on the surface COOH

groups, as follows:

$$HAC\text{-}COOH + CrO_4^{2-} = HAC\text{-}COOH\cdots CrO_4^{2-} \quad (2\text{-}26)$$

The encouraged capability of HAC on Cr(VI) sequestration was dominantly contributed by the increased surface oxygen-containing functional groups and the refined particle size in the presence of higher surface area. Meanwhile, the reduction of surface oxygen-containing functional groups was verified by the results obtained from Raman spectra and Boehm's titration. Additionally, the adsorption thermodynamic revealed that the spontaneity of Cr(VI) adsorption on HAC increased after ball milling. Fig. 28 shows a schematic representation of the increase in functional groups on the AC after high-intensity grinding and the adsorption of the chromium species on the functional groups.

2.3.7 Reusability and regeneration of HAC

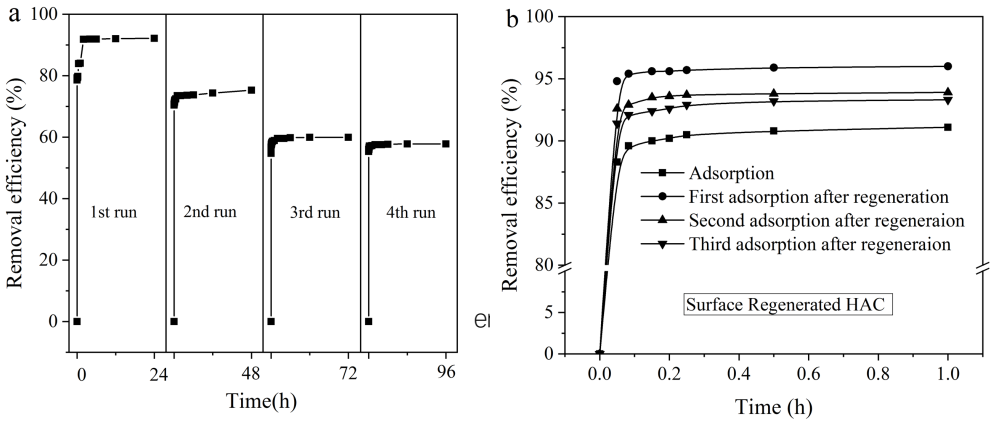

Figure. 2-13 The (a) reusability and (b) regeneration of HAC under pH 7.0 (5 g/100ml HAC, 1000mg/L Cr(VI), 295K)

Fig. 2-13(a) shows the Cr(VI) removal efficiency of HAC as a function of time subjecting the HAC to several consecutive adsorption runs at pH 7, the HAC was recycled to the next adsorption step without removing the loaded chromium. Cr(VI) removal was 92% when the HAC first contacted the Cr(VI) aqueous solution. This removal efficiency decreased steadily with the number of adsorption cycles, being 75% for the first cycle and 60% and 57% for the following. As noted in Figs 2-4 and 2-5, $Cr(OH)_3(s)$ is reported in the HAC pores and as a layer on the HAC surface. It follows

that $Cr(OH)_3(s)$ was definitively responsible for this decrease in removal efficiency as the number of cycles increased. The $Cr(OH)_3(s)$ blocked off the diffusion of Cr(VI) to the interior of the HAC particle. As noted in Fig. 2-11, at acid conditions, soluble Cr^{3+} is the predominant species, so with an acid wash, it is expected that the $Cr(OH)_3(s)$ in the pores and surface of the HAC will be removed leaving a particle with a free path for diffusion and further adsorption of Cr(VI). This was confirmed by subjecting the Cr loaded HAC to an acid wash then the regenerated HAC was subjected to another cycle of adsorption. Fig. 2-13(b) shows that the removal efficiency of Cr (VI) by HAC increased from 92.2% to 96.3% after acid regeneration. The uptake efficiency of Cr(VI) on HAC decreased with the recycling due to the formation of $Cr(OH)_3(s)$ as foregoing discussed.

2.4. Conclusions

The density of surface functional groups of activated carbon can be significantly improved by high-intensity grinding. Thus, the sequestration capability of commercial AC on Cr(VI) increases, and the removal of aqueous Cr(VI) can be undertaken under near-neutral pH. The feasibility and potential of HAC modified by ball milling on the practical application were developed. Besides, carrying out the Cr(VI) adsorption at near-neutral pH leads to the formation of $Cr(OH)_3(s)$ on HAC. $Cr(OH)_3(s)$ can be easily removed off by acid washing through which the HAC surface is regenerated and thereby regains its original adsorption capacity, and can be recycled to the Cr(VI) adsorption step. Once the adsorbent material has been regenerated, it can be used up to three stages without significantly losing its absorption capacity. The results obtained in this work showed that Cr(VI) adsorption of HAC at near-neutral pH proceeds through two mechanisms. One mechanism is the reduction of Cr(VI) to Cr(III) and hydrogen bonding of CrO_4^{2-} with COOH surface functional groups, and another is the Cr(III) precipitation to $Cr(OH)_3(s)$ in pores and surface of the HAC. This $Cr(OH)_3(s)$ could be removed by acid washing of the HAC, while the $Cr_2O_4^{2-}$ was removed by alkaline washing of the HAC. The studies of adsorption kinetic and isotherm show that the

Pseudo-second order model and Freundlich fitted the adsorption data well, implying the chemisorption and multi-layer adsorption of Cr(VI) on HAC and AC. The intraparticle model study confirmed that the transfer rate of Cr(VI) from the bulk solution to the surface of AC was increased after ball milling. The thermodynamic study indicated that the adsorption of Cr(VI) by HAC and AC is endothermic and the spontaneity of Cr(VI) adsorption on HAC was higher. The Work is yet needed to further improve the removal efficiency of the HAC for its recycling. This involved determining the performance of the HAC after a two-step treatment of the Cr-loaded HAC, under acidic and alkaline conditions.

Chapter III. **A new insight into the restriction of Cr(VI) removal performance of activated carbon under neutral pH condition**

3.1. Introduction

Chromium abounds in nature and is highly toxic in the form of CrO_4^{2-} and $Cr_2O_7^{2-}$ through bioaccumulation [519]. The chromium pollution of water, land, and environment has attracted the interest of experts as electroplating plants, stainless steel manufacturing plants, leather manufacturing plants, and refractory plants have progressively appeared [417, 520, 521]. Cr(III) presents less mobility, toxicity, and solubility than Cr(VI) and generates sparingly soluble chromium hydroxides [522]. The reduction of Cr(VI) to Cr(III) is rapid at acidic conditions, meanwhile, the readily available electron is required for the reduction process [523, 524]. It is well known that removing Cr(VI) from water by reduction and precipitation is a viable option [447, 525-527]. Conventional reducing agents are sulfur and iron salts [528, 529], post-treated effluent contained sulfate, and iron salts would contaminate water and soil. Furthermore, the mandatory wastewater discharge would result in high costs.

The bulk of published studies on Cr(VI) removal by low-cost and readily accessible activated carbon (AC) demonstrated that removal capacity was greater in acidic conditions than alkaline conditions. This suggests that the Cr(VI) elimination is strongly pH-dependent [27, 48, 530]. The removal efficiency of Cr(VI) by activated carbon prepared from teakwood sawdust was 100% at pH 2 while it was below 20 % at pH 10 [531]. Table 3-1 shows the capacity of several ACs to remove Cr(VI) in acidic and alkaline environments. At low pH, the removal capacity was favored because the positively charged surface of Cr(VI) advanced the adsorption of anion Cr(VI) [532]. It is worth noting that the pH-speciation of Cr(VI) reveals that $HCrO_4^-$ dominated below pH 6, whereas CrO_4^{2-} dominates above pH 7 [533]. Furthermore, prior studies have found that positively charged AC produced by protonation at a low pH value tends to attract chromate anions, which is thought to be the main mechanism for Cr(VI) adsorption [534]. It was discovered that as pH dropped, the reduction and adsorption process enhanced

simultaneously.

Table 3-1 Comparison of Cr(VI) removal under different pH by various carbon materials

Carbon materials	Cr(VI) removal capacity (mg/g)		Refs
	Acid condition	Alkali condition	
AC derived from *Posidonia Oceanica* seagrass	30.5 (pH 3)	0 (pH > 4)	[535]
Biochar derived from corn straw	125(pH 2)	50 (pH 6)	[536]
Powdered AC	46 (pH 2)	8 (pH 7)	[491]
Biochar derived from waste glue residue	206.7 (pH 2)	90 (pH 6)	[537]
AC prepared by calcination wheat bran	22 (pH 2)	0 (pH 10)	[538]
Commercial AC	21 (pH 2.5)	13 (pH 5.5)	[539]
KOH activated porous corn straw	98.3 (pH 3)	33.7 (pH 7)	[45]
AC derived from an acrylonitrile-divinylbenzene copolymer	80 (pH 2)	9 (pH 8)	[540]

To our understanding, there have been few investigations on systematic chromium adsorption and reduction study when pH rises over 7, to shed light on a substantial drop in AC performance. Most studies have only focused on the unfavorable effect of electrostatic repulsion between chromate anions and negatively charged AC surface at high pH values [45, 504, 541]. Besides, an earlier study failed to elucidate the removal paths at pH higher than 6 because the surface negatively charged bamboo bark-based AC that unfavored the adsorption of Cr(VI) anions, hence the reduction process of Cr(VI) to Cr(III) at high pH was omitted [542]. Cr(III) speciation as a function of pH was depicted

clearly by Lopez-Valdivieso's study showing that $Cr(OH)_3(s)$ predominates at pH over 6.4 [303]. The effect on the removal of Cr(VI) under alkaline conditions of the AC surface loaded Cr(III) precipitate was especially neglected. Early reported studies on the synthesis of eskolaite (α-Cr_2O_3) nanoparticles through AC following adsorption of Cr(VI) have shown that Cr_2O_3 was the reduced species of Cr(VI) on AC [469, 543]. Recently study showed that the Cr_2O_3 reduced the adsorption rate of Cr(VI) significantly [468].

Compared to the consensus that the electrostatic repulsion led to the poor Cr(VI) removal efficiency of AC at alkaline conditions, the effect of AC surface coated Cr_2O_3 precipitate on removal performance was not fully understood. This work aimed to study the effect of powdered AC (PAC) surface formed Cr_2O_3 precipitate on Cr(VI) removal, SEM-EDX (scanning electron microscope-energy dispersive X-ray analysis), and XPS (X-ray photoelectron spectroscopy) were used to investigate the surface morphology and the chemical properties. Desorption and regeneration experiments were used to confirm the role of Cr_2O_3. The insight gained from this study would help to expand the longevity of AC and the recovery of Cr via AC.

3.2. Materials and methods

3.2.1. Characterization of PAC particle

To scrutinize the composition of loaded-chromium on PAC after Cr(VI) removal, three types of de-passivation agents were examined to desorb the adsorbed/reduced chromium on PAC. The formation process of the chromium layer on PAC at pH 3 and 7 was inspected by carrying out consecutive desorption tests following each Cr(VI) adsorption. SEM-EDX (JSM-6610LV, JEOL, Japan) and XPS (K-Alpha, Thermo Scientific, USA) were employed to characterize the distribution of chromium and the chemical species of Cr and C on PAC at pH 3 and 7, respectively. The difference of removal mechanisms under the two pH values was delineated by XPS and Raman spectroscopy (DXR, Thermo Scientific, USA).

3.2.2. Materials

All the chemicals were analytical grade and the aqueous solutions were prepared with deionized water through Barnstead pure II water purification system (Thermo Scientific, USA). Potassium dichromate ($K_2Cr_2O_7$) was purchased from J.T.Baker and used for preparing 1000 mg/L Cr(VI) as a stock solution. 1.0 M H_2SO_4 and 1.0 M NaOH were used to adjust the pH of the aqueous solutions. H_2SO_4, NaOH, KCl, and 1,5–diphenylcarbazide were provided by J.T.Baker. Commercial available AC was provided by Calgon company, its chemical composition was 97% carbon and 3% inorganic residual. The AC was treated by ball milling and obtained a PAC with an average size of 4 μm, a specific surface area of 929 m^2/g, and a pore radius of 15.9 Å, PAC used in this study was reported in our previous work [523]. Following the grinding step, the PAC was dried and stored in a desiccator.

3.2.3. Comparison of Cr(VI) removal at different pH

A comparison was conducted for the PAC removal efficiency at pH 3, 7, and 9 [544]. The desired mass of PAC (5 g) was mixed with deionized water (100 mL) for 1 h, then the pH was adjusted to 3, 7, and 9 using 1.0 M H_2SO_4 and NaOH aqueous solutions and monitoring the pH with an Orion 3 star pH meter (Thermo Scientific, USA). 0.2829 g $K_2Cr_2O_7$ reagent was added to the PAC suspension to prepare a 1000 mg/L solution once the pH was stable. To follow the Cr(VI) uptake a 200 μL aliquot was withdrawn from the aqueous solution at 3, 5, 9, 15, 30, 60, 360, 1440 min. The withdrawn aliquot was centrifuged in a centrifuge (Allegra^{TM} 21, Beckman coulter, USA) for 15 min prior to analysis. The Cr(VI) removal capacity was calculated through Eq (3-1) [545], wherein Γ(mg/g) is the removal capacity, C_0 (mg/L) is the initial concentrations and C_t is the concentration at time t, V (L) and M (g) are the volume of solution and dose of PAC, respectively.

$$\Gamma = (C_0-C_t)V/M \quad (3\text{-}1)$$

3.2.4. Selection of desorption agents

Three kinds of desorption agents were evaluated to determine their effectiveness for desorbing the adsorbed chromium species on PAC. Analytical grade $K_2Cr_2O_7$ acted as a precursor of the chromium layer on PAC. To obtain adequate loaded chromium on PAC for assessment, consecutive uptake experiments were undertaken. 5.0 g PAC was mixed with 1000 mg/L Cr(VI) aqueous solution at a fixed pH of 7 in a glass volumetric flask. This suspension was stirred magnetically (Thermo scientific, USA) at 100 rpm to prevent deteriorating of the chromium layer formed on the PAC. A 200 μL sample was withdrawn from the suspension at 0.25, 0.5, 1, 3, 5, 7, 9, 12, 15, 30, 60, 120, 1440 min to determine the concentration of Cr(VI), then the suspension was filtered to collect the PAC, which was rinsed with deionized water, and dried before the following removal experiments. Consecutive removal steps were performed with 1000 mg/L Cr(VI). Dried chromium-load PAC after four repetitive adsorption runs was used for the desorption testing. All the batch experiments were conducted in duplicate under ambient conditions. The adsorption capacity at equilibrium for Cr on PAC was expressed as Eq (3-2)

$$q_p = \sum(1000-Ce_i)V_i/M_i \quad (3\text{-}2)$$

where q_p (mg/g) is the content of chromium on PAC, Ce_i (mg/L),V_i (mL) and M_i (g) (i=1, 2, 3, 4) are the equilibrium concentration, solution volume and mass of PAC of each removal cycle, respectively.

To desorb the loaded chromium from the PAC, 0.2M KCl, 0.2M H_2SO_4, and 0.1M NaOH were employed. 0.5g chromium-loaded PAC was mixed with 50 ml of the desorption agent solution in a glass volumetric flask and stirred at 200 rpm, the concentration of desorbed chromium after 1, 3, 5, 7, 9, 24, 30, 48, 72, 96, 148 h was determined, the efficiency of desorption was determined through Eq (3-3).

$$\eta = 100 \times (C_t\, V)/(q_p\, M) \quad (3\text{-}3)$$

where η (%) is desorption efficiency, C_t (mg/L) is the dissolved chromium concentration at t time, V (L) and M (g) are the volumes of desorption solution and dose of PAC correspondingly. In addition, the performance of PAC treated with Cr(VI) after desorption with different chemical agents was evaluated.

3.2.5. The formation process of chromium layer at pH 3 and 7

To ascertain the route of the chromium layer formed on PAC, the chromium speciation after consecutive adsorption runs was analyzed with selected desorption agents (0.2M H_2SO_4 and 0.1M NaOH solution). Four desorption tests followed four successive removal cycles were performed and the increment content of loaded chromium on PAC between two successive adsorption runs was determined by Eq (3-4).

$$\Delta q = (C_{ii} - C_i)V/M \quad (3\text{-}4)$$

where Δq (mg/g) is the increased content of chromium on PAC, C_{ii} and C_i (mg/L) are the equilibrium concentration of desorbed chromium after the two successive elution tests, V (ml) and M (g) are the volume of desorption solution and the dose of PAC after adsorption of Cr(VI).

The adsorption capacity of PAC loaded with chromium on Cr(VI) after the last elution assessment was examined, and all the adsorption experiments were conducted with 1000 mg/L Cr(VI).

3.2.6. Analytical method

A colorimetric approach employing 1,5–diphenylcarbazide and a UV-Visible spectrophotometer (Thermo Scientific, USA) coupled with a 1 cm quartz cell was used to determine Cr(VI). 100 μL filtered solution was diluted to 10 ml and mixed with 0.1 mL 49% H_2SO_4, 0.1 mL 42.5% H_3PO_4, and 0.4 mL 0.2 % 1,5–diphenylcarbazide solution, sequentially. The mixed solution stood for 10 min and was then measured by a UV-Visible spectrophotometer under 540 nm. The absorbance of deionized water was used as a reference. With prepared 0, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L Cr(VI), a standard curve of concentration versus absorbance was constructed, this standard curve was used to determine the Cr(VI) concentration of the sample. The total concentration of aqueous Cr was analyzed by atomic absorption spectrometry (AAS, Varian Spectra 220FS), a 50μL filtered solution was diluted to 10 mL and then sprayed into the flame of air-acetylene. The chromium ground state atoms formed under a high-

temperature flame produce selective absorption of the 357.9 nm characteristic spectrum of chromium hollow cathode lamps, and the absorbance value is proportional to the concentration of Cr. The standard curve of total Cr was built in the same way as Cr(VI), and the concentration of total was determined by the standard curve as well. The presence of soluble Cr species in the solution was Cr(III) and Cr(VI), the concentration of aqueous Cr(III) was confirmed by the difference between total Cr and Cr(VI).

3.3. Results and discussion

3.3.1 Particle characterization

3.3.1.1 Surface morphology

The surface morphology of PAC after Cr(VI) adsorption under pH 7 was characterized by SEM-EDX and elements mapping. As seen in Fig.3-1, a chromium layer adsorbed mostly on the PAC surface. A similar observation was reported recently [468].

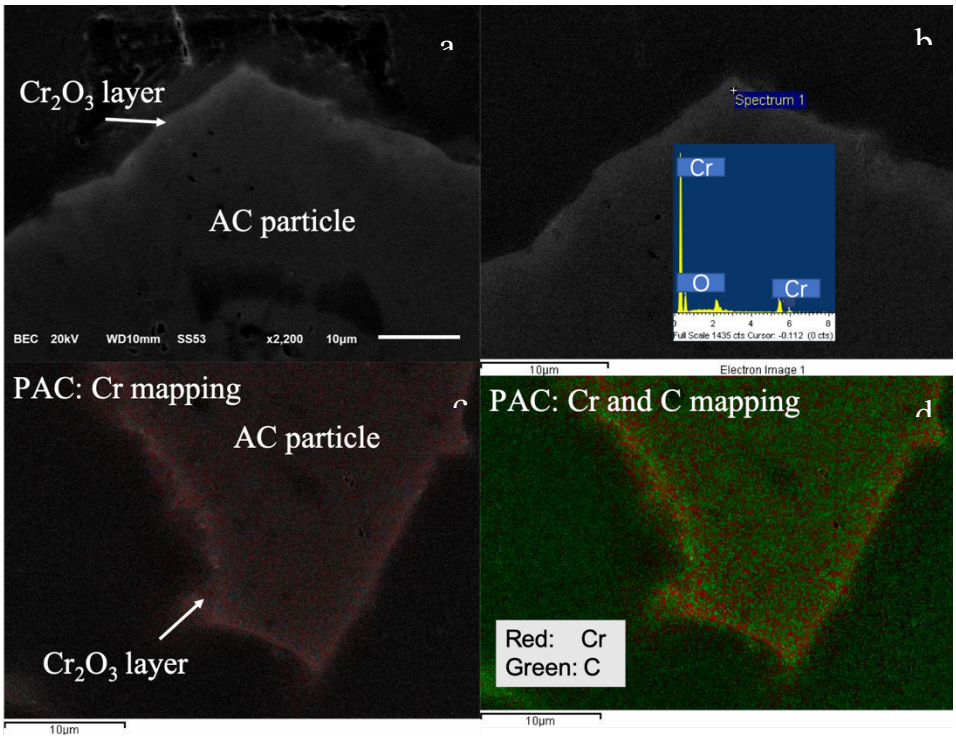

Figure. 3-1 SEM-EDX micrographs (a and b) and SEM coupling with elements mappings (c and d) of PAC after Cr(VI) adsorption at pH 7.

3.3.1.2 XPS spectra analysis

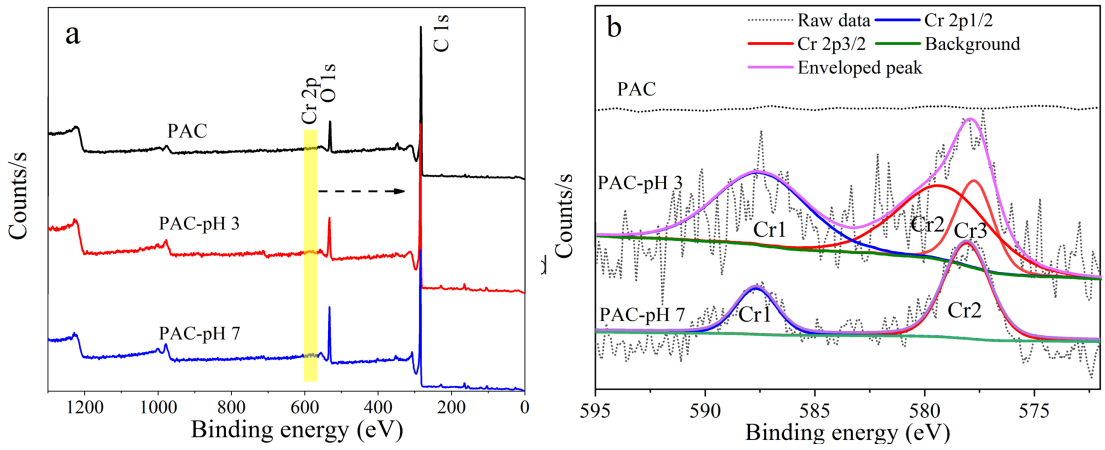

Figure. 3-2 The XPS spectra of PAC treated with Cr(VI) under pH 3 (PAC-pH 3), pH 7 (PAC-pH 7), and fresh PAC; (a) XPS survey, (b) scan of Cr 2p

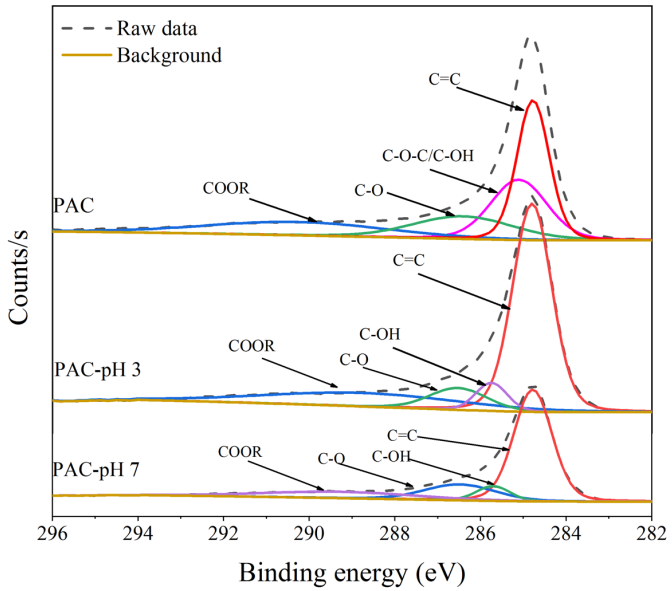

Figure. 3-3 High resolution C 1s spectra of PAC, PAC-pH 3, and PAC-pH 7.

To further inspect the chemical species of Cr on the surface of PAC, the XPS analysis was employed. Figs 3-2(a) and (b) showed the XPS spectra, which were fitted and deconvoluted into multiple peaks by CasaXPS (version 2.3.23). The peak referenced as C 1s at 284.8 eV, the Shirley type was designated as the background subtraction. As presented in Fig. 3-2(a), the Cr 2p peak due to Cr(VI), denoted that the Cr(VI) was adsorbed onto PAC. The XPS spectrum of PAC after being treated with Cr(VI) at pH 3 (PAC-pH 3) and 7 (PAC-pH 7) was built as presented in Fig.2(b). The

Cr 2p region of the photoelectron spectrum was both detected for PAC-pH 3 and PAC-pH 7, which was consistent with the EDX spectrum shown in Fig. 3-1. Cr 2p involves two energy levels, 2p 1/2 and 2p 3/2. The XPS spectrum of PAC-pH 3 can be divided into the Cr1, Cr2, and Cr3 peaks, where the binding energies (BE) value of Cr1 peak of PAC-pH 3 was 587.5 eV, which was very close to that of Cr_2O_3 (587.4 eV ± 0.2) [546]. The BE for Cr2 and Cr3 of PAC-pH 3 were 579.2 and 577.8 eV, respectively, which can be attributed to Cr(VI) [547-549]. Two contributions of Cr1 and Cr2 for the Cr 2p region of PAC-pH 7 were 587.7 and 578.0 eV, matching well with the binding energy for Cr(VI) and Cr_2O_3 [549-551]. Due to XPS detection depth was no more than 4 nm from the sample surface, it can be said that the chromium layers on the surface of PAC-pH 3 were mainly constituted by Cr(VI) and PAC-pH 7 was mainly constituted by Cr_2O_3(s) [552]. Consistent with the present results, previous studies have demonstrated that the reduction and adsorption participated principally in the Cr(VI) removal on biomass [553, 554]. Moreover, the peak area ratio (Cr1 versus total peaks) as determined by CasaXPS was 69.93% and 39.91% Cr_2O_3(s) on the surfaces of PAC-pH 7 and PAC-pH 3, respectively. This higher content of Cr_2O_3 on PAC-pH 7 clearly evidenced that more Cr_2O_3 formed on the PAC at pH 7 than at pH 3, impeding the diffusion of Cr(VI) into the PAC, leading to a lower level of Cr(VI) removal. Besides, the ratio of O/C on PAC, PAC-pH 3, and PAC-pH 7 were 0.075, 0.113, and 0.157, respectively (Table 2). This indicates more O on the PAC after adsorption at pH 7 than at pH 3, due to more Cr_2O_3 precipitate. As noted in Table 3-2, the ratio of Cr/C on PAC-pH 3 was higher than that on PAC-pH 7, which further substantiated that Cr(VI) removal efficiency under pH 3 was superior to that under pH 7 and indicated that not only there was Cr_2O_3 on the PAC surface but also Cr(VI).

Table 3-2 XPS analysis of PAC before and after treatment with Cr(VI)

Materials	O/C	Cr/C
PAC	0.075	0
PAC-pH 3	0.113	0.005
PAC-pH 7	0.157	0.004

The surface functional groups of PAC before and after Cr(VI) adsorption were investigated using high resolution C1s spectra. The deconvolution of C 1s produced four peaks, as shown in Fig. 3-3. For PAC, there were four components: C=C (284.8 eV), C-O-C/C-OH (285.5 eV), C-O (286.7 eV), and COOR (286.7 eV) (290.0 eV) [555]. Similarly, the four peaks of PAC-pH 3 were assigned to the C=C (284.8 eV), C-OH (285.8eV), C-O (286.5 eV), and COOR (288.7 eV) [556, 557]. Meanwhile, the four peaks for PAC-pH 7 were allocated to C=C (284.8 eV), C-OH (285.8eV), C-O (286.5 eV), and COOR (289.5 eV) [558]. The relative percentages of C-OH for PAC, PAC-pH 3, and PAC-pH 7 were 23.62%, 6.77%, and 6.53%, respectively, which suggested that the group of C-OH contributed to the removal of Cr(VI). The oxidation of C-OH to C-O by Cr(VI) caused the increase of the C-O group [460]. Nonetheless, following Cr(VI) adsorption at pH 3, the relative percentage of COOR on PAC rose from 15.22% to 20.56% and dropped to 10.41% after Cr(VI) adsorption at pH 7. This inconsistency may be due to Cr(VI) oxidized the surface of PAC at pH 3 and introduced more COOR groups [559], while the Cr(VI) exhibited weak oxidative capacity at higher pH [560], and the removal of Cr(VI) under pH 7 consumed the COOR groups through the complex.

3.3.1.3 Raman spectra analysis

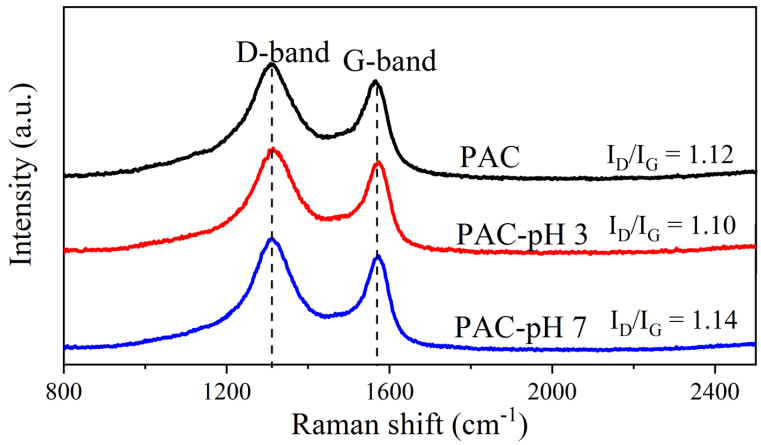

Figure. 3-4 Raman spectra investigation for pristine PAC, after removal of Cr(VI) at pH 3 and 7.

Raman spectroscopy investigation was carried out to evaluate the degree of structural order in carbonaceous PACs, as well as to investigate the difference in Cr(VI) removal mechanisms at pH 3 and pH 7. As depicted in Fig. 3-4, the two sharp and

strong bands are associated with the D-band (1319cm^{-1}. defect with sp^3 bonding) and G-band (1563cm^{-1}, graphitization with sp^2 bonding) [488]. The intensity ratio of D-band (I_D) versus G-band (I_G) is often used to assess the degree of disorder in graphite structure in carbon materials [561]. The value of I_D/I_G declined from 1.12 to 1.10 after treatment at pH 3 but increased from 1.12 to 1.14 after treatment at pH 7. As a result, the existence of defects in PAC was strengthened under pH 7, while at pH 3, a well-organized carbon structure formed. This divergence could be explained by the different Cr(VI) adsorption mechanisms at pH 3 and 7. In general, the reduction of surface oxygen-containing functional groups resulted in the increase of amorphous carbon at pH 7 [490, 492, 562, 563], while the oxidation of hybridized carbon atoms caused structural order to grow at pH 3 [564].

3.3.2. Adsorption performance of PAC at pH 3 and 7

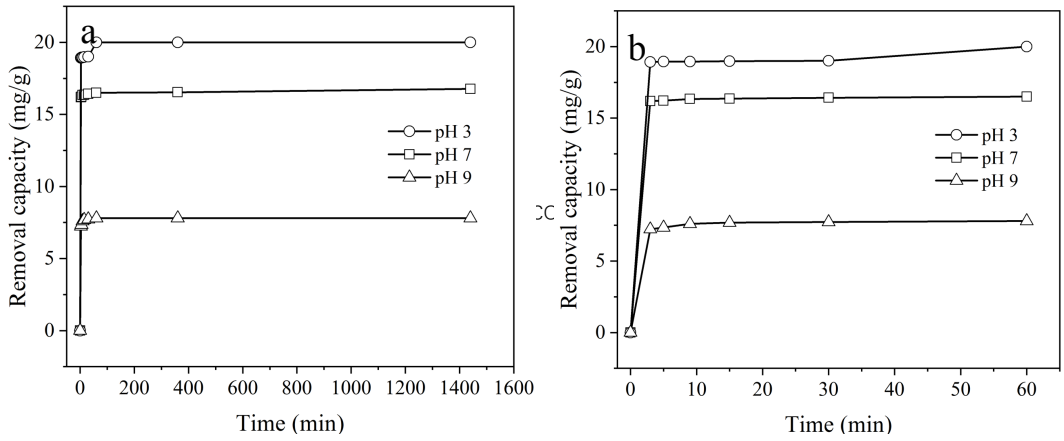

Figure. 3-5 The adsorption capacities comparison at pH 3, 7, and 9, (a) the full profile of adsorption, (b) the first 60 min adsorption profile (Initial concentration 1000 mg/L, 50g/L PAC, 295K)

Fig. 3-5 shows a comparison of adsorption performance at pH 3, 7, and 9 for 1000 mg/L initial concentration of Cr(VI). Adsorption at those three pH values both reached pseudo-equilibrium immediately after 10 mins. Removal capacities for PAC at pH 7 and 3 were 16.8 mg/g and 20 mg/g, respectively, equivalent to 83.86% and nearly 100% removal efficiency. And adsorption capacity under pH 9 was 7.8 mg/g which was much lower than that at pH 3 and 7. It indicated that the removal performance of PAC on

Cr(VI) was higher at low pH, PAC is probably protonated and attracted more anionic Cr(VI).

3.3.3. Desorption performance of Cr-loaded PAC with chemical agents

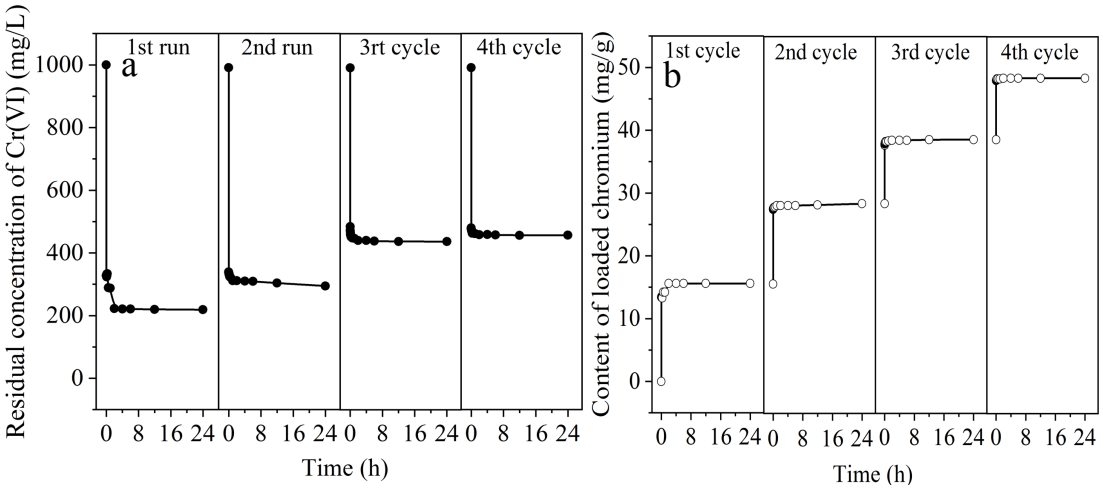

Figure. 3-6 The preparation of chromium-loaded PAC, (a) The residual concentration of Cr(VI) at each Cr(VI) adsorption cycle, (b) the content of loaded chromium as cycling (1000mg/L Cr(VI), 295K, 50g/L, pH 7)

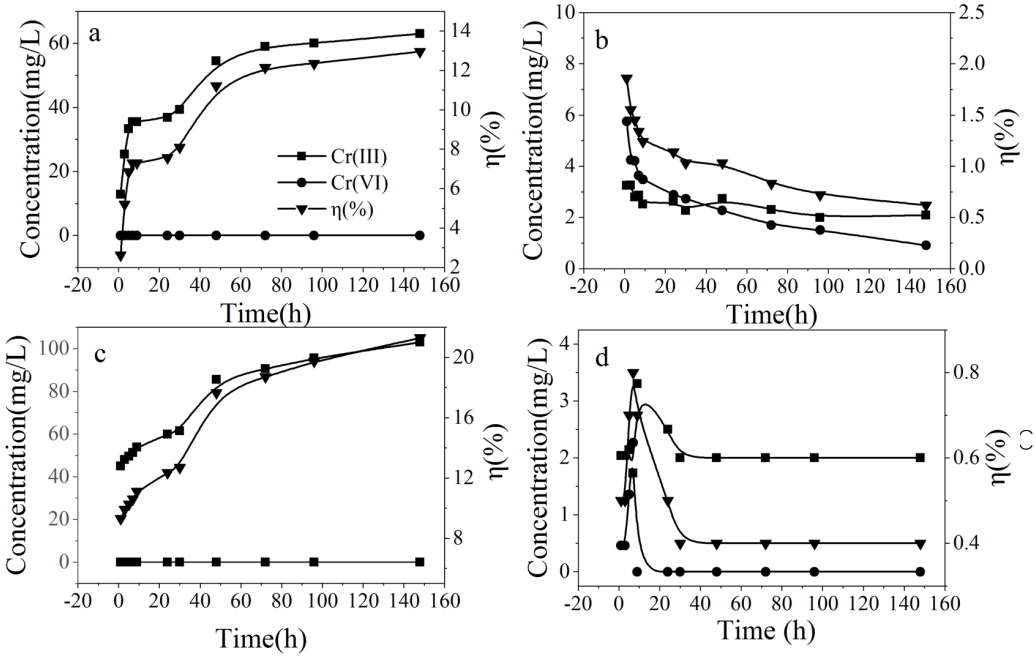

Figure. 3-7 The effect of chemical agents on desorption performance of Cr-loaded PAC (a) H_2SO_4 (b) KCl (c) NaOH (d) H_2O (0.2M KCl, 0.2M H_2SO_4, 0.1M NaOH, 1g/100mL Cr-loaded PAC, 298K)

The desorption of chromium from the Cr-loaded PAC was evaluated using various chemical agents including H_2SO_4, KCl, and NaOH. Abundant chromium-loaded PAC was prepared at pH 7. As shown in Fig. 3-6, the Cr(VI) elimination experiment using PAC was repeated four times. The duration time for every removal cycle was 24 hours. The next removal cycle began once the previous cycle was completed. After four consecutive repetitive adsorption cycles, the content of chromium on PAC reached 48.6mg/g. The results of the desorption analysis using the three reagents are shown in Fig. 3-7. It is noted that only Cr(III) was dissolved in H_2SO_4 aqueous solutions, whereas Cr(VI) was only desorbed in NaOH aqueous solutions. Negligible Cr(III) or Cr(VI) were detected in the KCl solution when compared to acidic and alkaline aqueous solutions. These findings agree well with Ouki and Neufeld's (1997) findings that 3 g/L Cr(III) and 8.4 g/L Cr(VI) were recovered when exhausted carbon was regenerated under acidic and alkaline conditions, respectively [565]. Due to the great stability of the adsorbed chromium on the PAC, desorption of Cr(VI) and Cr(III) from the Cr-loaded PAC with deionized water was minimal. Our results are also in line with those of Jing et al. (2011), who found that the desorption rate of Cr-loaded AC was low with distilled water [566].

As shown in Fig. 3-7(a), Cr(III) precipitate dissolved gradually in 0.2 M H_2SO_4, and 13.0 % Cr(III) precipitate was removed under acidic conditions, this process was depicted by Eq (3-5).

$$Cr_2O_3 + 6H^+ \rightarrow 2Cr^{3+} + 3H_2O \qquad (3\text{-}5)$$

With the NaOH aqueous solution (Fig.3-7 (c)), 21.3 % Cr(VI) was desorbed, which was higher than the dissolved Cr(III) by the H_2SO_4 aqueous solution. This seems to contradict the XPS conclusion that less Cr(VI) adsorbed on PAC-pH 7 surface. A possible explanation for this might be that more internal adsorbed Cr(VI) in PAC particles were desorbed by alkaline elution. Cr(VI) adsorbed on AC was previously shown to be bound to the surface functional groups [567]. An ion-exchange mechanism could explain the desorption of adsorbed CrO_4^{2-} (the dominant chromium species under alkaline conditions) on surface functional groups by NaOH aqueous solutions, the OH^-

ions substitute for CrO_4^{2-} anions, as demonstrated in Eq (3-6) [568].

$$PAC\text{-}(COOH_2^+)_2\cdots CrO_4^{2-}\ (s) + 2OH^- \rightarrow PAC\text{-}(COOH)\ (s) + CrO_4^{2-} + H_2O \quad (3\text{-}6)$$

These findings could be useful in the development of a selective recovery method of Cr(III) and Cr(VI) using acid and alkali aqueous solutions.

3.3.4. Formation process of chromium layer at pH 3 and 7

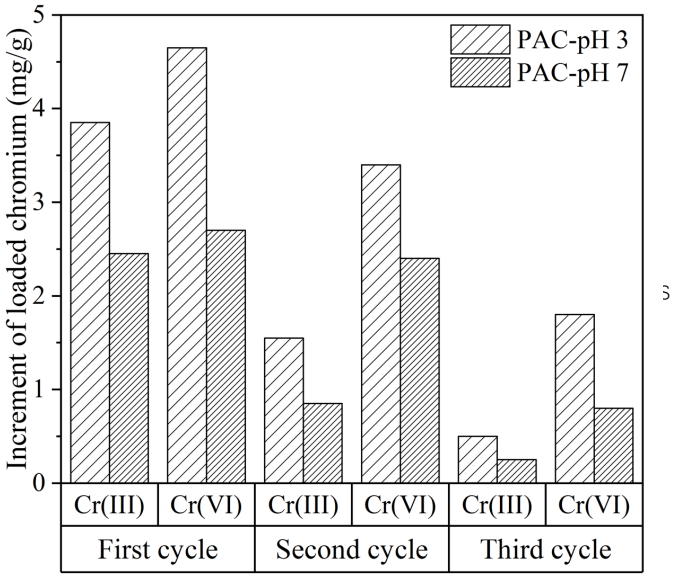

Figure. 3-8 The increment of chromium loaded on PAC as consecutive Cr(VI) removal cycle (295K, 50g/L)

To clarify the influence of pH on the development process of chromium layer on PAC, H_2SO_4, and NaOH desorption agents were used to determine the content of Cr(III) and Cr(VI) adsorbed on PAC-pH 3 and PAC-pH 7. Fig. 3-8 compares the results obtained from elution tests of PAC-pH 3 and PAC-pH 7 after three consecutive adsorption cycles. It is apparent from the figure that the increment of adsorbed Cr(VI) is higher than reduced Cr(III) at each cycle for both PAC-pH 3 and PAC-pH 7. Hence it is conceivable to suggest that the adsorption process prevailed for Cr(VI) elimination. This finding was also reported by Daneshvar et al. (2019) [568]. Another significant observation was that for PAC-pH 3 and PAC-pH 7, the adsorbed Cr(VI) and reduced Cr(III) decreased as the cycles progressed. PAC-pH 3 showed higher Cr(VI) adsorption and reduction capacity. This may be due to the more generated Cr(III) precipitate

accumulating on the PAC surface over time at the neutral condition, sheltering the PAC active sites from Cr(VI adsorption.

3.3.5. Performance of Cr-loaded PAC after desorption

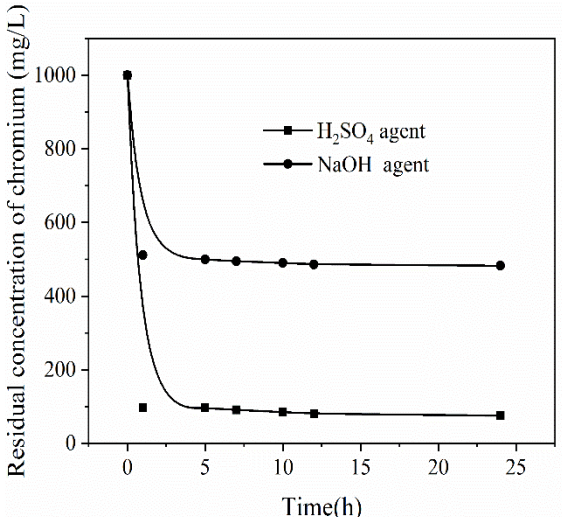

Figure. 3-9 The activity of chromium-loaded PAC-pH 7 after treated with H_2SO_4 and NaOH (1000mg/L Cr(VI), pH 7)

The performance of the PAC for Cr adsorption was assessed after chromium was desorbed from the PAC using the H_2SO_4 and NaOH. Re-adsorption experiments were conducted following the third cycle desorption step. As can be seen in Fig. 3-9, 92.43% removal efficiency of Cr(VI) was achieved by PAC-pH 7 after washing with H_2SO_4, whereas only 51.72% removal was attained using NaOH aqueous. Therefore, it can be inferred that the Cr(III) precipitate is mainly responsible for the poor performance of PAC under neutral conditions. The removal performance after acid washing (92.43%) was higher than the preliminary removal efficiency (83.86%); this result indicated that the acid desorption procedure modified PAC properties and introduced surface functional groups. These results are consistent with those of Guolin Huang et al. (2009), who improved AC's Cr(VI) removal capacity by modifying it with nitric acid [463]. As a result, it is proved that PAC's limited removal capability for Cr(VI) at pH 7 was mostly due to Cr(III) precipitate that formed on the surface of PAC. This finding backs with the XPS results in that chromium oxide piled up mostly on PAC under neutral

conditions. The sulfuric acid proved to be a potential chemical agent for the regeneration of Cr-loaded PAC after treating water contaminated with Cr(VI).

3.4. Conclusions

This study aimed to determine the mechanism of the limited sequestration capability of PAC on Cr(VI) under neutral conditions compared to acidic conditions. SEM-EDX substantiated that a chromium layer was formed on PAC, while XPS spectra corroborated the higher Cr_2O_3 content on PAC under alkaline conditions, resulting in poor Cr(VI) removal performance. Conversely, a lower Cr_2O_3 content on PAC under acid conditions is related to the higher Cr(VI) removal capacity. Desorption tests with H_2SO_4 and NaOH solution revealed that the precipitated Cr_2O_3 and adsorbed Cr(VI) can be selectively desorbed, proving that adsorption and reduction processes contributed significantly to the Cr(VI) removal. Consecutive desorption assays proved that the reduction and adsorption capability at 7 declined with time and were both lower than at pH 3. This is due to Cr(III) precipitate and adsorbed Cr(VI) blocking active sites. The superior performance on Cr(VI) removal of Cr-loaded PAC after desorption by H_2SO_4 further confirmed that the restricted removal performance under neutral conditions was ascribed to the formation of Cr_2O_3 passivation layer on the surface of PAC particle. The insights gained from this work may be of assistance to the recycling of chromium from exhausted AC and extend the lifespan of AC.

Chapter IV. **Conclusions**

The pronounced results of the Cr(VI) reduction and precipitation by modified activated carbon proved that the action of ball milling can refine the activated carbon particles and improve the surface area, meanwhile, the enriched surface functional groups accompanied the enhanced hydrophilicity took responsibility for the advanced Cr(VI) removal at neutral and alkaline conditions. The generated Cr(III) precipitated on the surface of activated carbon particles, the elution experiments and re-adsorption test proved that the surface Cr(III) oxides layer caused the low Cr(VI) removal efficiency at higher pH than that at low pH. Moreover, the reduction and adsorption process both declined as time. The activated carbon after treating with Cr(VI) could be rejuvenated by acidic washing and the capacity maintained satisfactory even after three times repetitive Cr(VI) treatment.

The inactivation of Fe^0 at high pH due to the passivation could be solved by the motion of ball milling, the surface formed Fe(III)/Cr(III) (hydro)oxides were peeled off and the fresh core Fe^0 exposed to the Cr(VI) aqueous. The Cr(VI) removal experiments conducted under different DO indicated that the anaerobic conditions mitigated the consumption of Fe^0 by competitive oxidant O^2 and the removal rate was the highest. The DO improve the depletion rate of Cr(VI) at the first segment through the generated Fe(II) by DO, but the Fe(II) ions were further oxidized by DO as pH increased and the removal rate decreased significantly. The analysis of XPS spectra denoted that reduction and precipitation dominant the elimination of Cr(VI) by Fe^0/Fe_2O_3 micro particles.

Appendix

Published Papers during Ph.D

1. **Fang Y**, Wu X, Dai M, et al. The sequestration of aqueous Cr (VI) by zero valent iron-based materials: From synthesis to practical application[J]. Journal of Cleaner Production, 2021: 127678. (Q1, IF 9.297) https://doi.org/10.1016/j.jclepro.2021.127678
2. **Fang Y**, Yang K, Zhang Y, et al. Highly surface activated carbon to remove Cr (VI) from aqueous solution with adsorbent recycling[J]. Environmental Research, 2021, 197: 111151. (Q1, IF 6.498) https://doi.org/10.1016/j.envres.2021.111151
3. **Fang Y**, Yang K, Zhang Y, et al. A new insight into the restriction of Cr (VI) removalperformance of activated carbon under neutral pH condition[J]. Water Science and Technology, 2021. (Q2, IF 1.915) https://doi.org/10.2166/wst.2021.449
4. **Fang Y**, Peng C, Yang K, et al. Adsorptive removal of cationic toxic dyes from aqueous solution: adsorbents development and performance investigation[j]. Fresenius Environmental Bulletin, 2020, 29(7 A): 6072-6081. (Q4, IF 0.489)

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