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NATIONAL UNIVERSITY OF SINGAPORE

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SYNTHESIS AND APPLICATION OF HYDROUS CERIUM OXIDE MODIFIED ACTIVATED CARBON FOR ARSENIC AND LEAD REMOVAL

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2014

Declaration

I hereby declare that the thesis is my original work and it has been written by me in its entirety.
I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

Zhang Chengyu

13 Aug 2014

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Summary

Heavy metal contamination in aqueous system has become global concern due to great threat to public health and environment. This study aimed to fabricate a novel carbon based adsorbent, hydrous cerium oxide modified activated carbon (HCO-AC), to remove two kinds of commonly existed heavy metal, arsenic and lead from aqueous system. A three-step synthesis approach was developed to fabricate the adsorbent which was easy-operated and cost effective. The successful fabrication had been verified by SEM image. Comparing with single hydrous cerium oxide (HCO) and cerium oxide modified carbon (CO-AC) that were also fabricated in our study, HCO-AC significantly improved the adsorption performance of arsenic, the adsorption capacity for As(V) and As(III) were increased to 46.18 mg/g and 36.93 mg/g, respectively. The fabricated HCO-AC also had a notable adsorption performance for Pb(II) removal, the adsorption capacity of which could also reach 48.52 mg/g. Pseudo-second order model could well describe the adsorption kinetics of HCO-AC for all of As(V), As(III) and Pb(II). The adsorption isotherm of all the adsorption process for arsenic and lead could be more accurately fitted by two-site Langmuir isotherm model derived from classic Langmuir model. HCO-AC could be utilized for efficient As(V) and As(III) removal in a wide pH range from 3 to 6 and 4 to 7, respectively, or be utilized as a kind of large adsorption capacity adsorbent for Pb(II) removal in slight acid pH condition from 5 to 6. The presence of several commonly coexisting anions or cations did not have significant influence on the adsorption capacity of HCO-AC for arsenic and lead, respectively. The presence of natural organic matter (NOM) in aqueous system could induce negative potentials as well as a variety of organic groups onto the surface of HCO-AC, which competed with arsenic adsorption, but also improved the adsorption capacities of Pb(II) by contrast. According to the remarkable adsorption performance, HCO-AC fabricated in this study provided a promising, convenient, and multifunctional treatment option for efficient removal of As(V), As(III) and Pb(II) from heavy metal contaminated water.

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Chapter 1

Introduction

1.1 Background

Heavy metals are found naturally and ubiquitously in the earth. Commonly encountered heavy metals are lead, arsenic, mercury, copper, nickel, cadmium etc., all of which are not biodegradable and tend to accumulate in living organisms. Because of their toxicity, carcinogenicity and mutagenicity, heavy metals may pose great threat to the ecosystem as well as public health. In the past few decades, an increasing number of heavy metals have been generated and discharged into the environment with the rapid development of industries, for example, common source are from mining industrial wastes and vehicle emissions, municipal effluent, agricultural runoff, electronic products, fertilizers, treated woods, batteries and so forth [1]. Since the existence of these hazardous metals in natural water sources has caused some famous pollution as well as epidemic cases in developed countries like Japan and United States, and has been increasingly detected in some developing countries like China, India and Bangladesh, standards and acts have been promulgated by the World Health Organization (WHO) and the government of countries to protect public health and natural resources. For instance, the Clean Water Act and its amendments have been promulgated by the United States Environmental Protection Agency (USEPA) in 1970s to protect the public from exposure to some of these undesirable and harmful heavy metals [2]. Similarly, WHO has inaugurated International Programme on

Chemical Safety, to establish the scientific basis for the sound management of chemicals, and to strengthen national capabilities and capacities for chemical safety. In this Programme, ten chemicals of major public health concern have been listed, including four kinds of heavy metals: arsenic, cadmium, lead and mercury, which emphasizes the importance of negative effect control and proper management of heavy metals [3]. Meanwhile, many countries have amended the national standards for drinking water to more stringently control the maximum contaminant level of heavy metals [4]. Among all the heavy metals, as two kinds of naturally widespread species in the environment, arsenic and lead are often introduced into drinking water supply and causing hazardous effects through various industrial sources, thus the effective removal of these two heavy metals is becoming an increasingly significant topic of research. In order to meet the upgrading regulations and standards, and manage the heavy metal waste more properly and efficiently, great efforts therefore have been devoted to develop more promising technologies to remove multiple heavy metals such as lead and arsenic from water in recent years.

1.2 Objectives and scopes

Compared with many conventional water treatment technologies for heavy metals, adsorption is regarded as a highly-efficient and cost-effective approach. This study aimed to develop effective and multifunctional adsorbents to remove As(V), As(III) and Pb(II) from aqueous system. The coordination structures as well as adsorption behavior were further examined by using spectroscopic techniques and batch adsorption experiments. The major goals were to:

(1) Develop a novel three-step synthesis approach to modify particle activated carbon with nanosized hydrous cerium oxide, to form a novel multifunctional adsorbent, HCO-AC, which is easy-operated and cost effective; Verify the surface structure of novel adsorbents by microscopy;

(2) Investigate the adsorption behavior of the adsorbent for As(V), As(III) and Pb(II) including kinetics and isotherms, employing different models to fit the experimental result, comprehensively describe the adsorption process according to model fitting, so as to achieve efficient removal of both hazardous cations and anions in contaminated water;

(3) Evaluate the effect of different factors in real circumstance for As(V), As(III) and Pb(II) adsorption performance, including the effect of solution pH, common coexisting anions, coexisting of natural organic matter (NOM) on the capacity of adsorption, try to provide a promising, convenient, and multifunctional treatment option for water remediation.

Chapter 2

Literature review

2.1 Status quo of arsenic and lead contamination

Arsenic is a chemical element places under group V A of periodic table, which has an atomic weight of 74.92. Arsenic has five oxidation states, among which As(V) and As(III) are the normal oxidation state for soluble aqueous complexes. As one of the biggest sources of water contamination [5], arsenic could be introduced into water by both natural and anthropogenic activities such as dissolution of minerals, manufacturing and mining [6]. Arsenic contamination of water especially groundwater has become a major problem around the world. Long-term drinking of arsenic contaminated water could result in serious health risks due to its high toxicity and carcinogenicity [7, 8]. Countries like Bangladesh have been under severe groundwater contamination from natural arsenic, majority of wells contain more than 50 μg/L of arsenic in about half of the countries' region (Fig. 2.1a) [9]. Many parts of China are known to have significant levels of arsenic in ground water (Fig. 2.1b) [10]. Widespread of skin lesions and cancer, peripheral neuropathy, diabetes, cardiovascular diseases are associated with extensive exposure to arsenic found in drinking water supply.

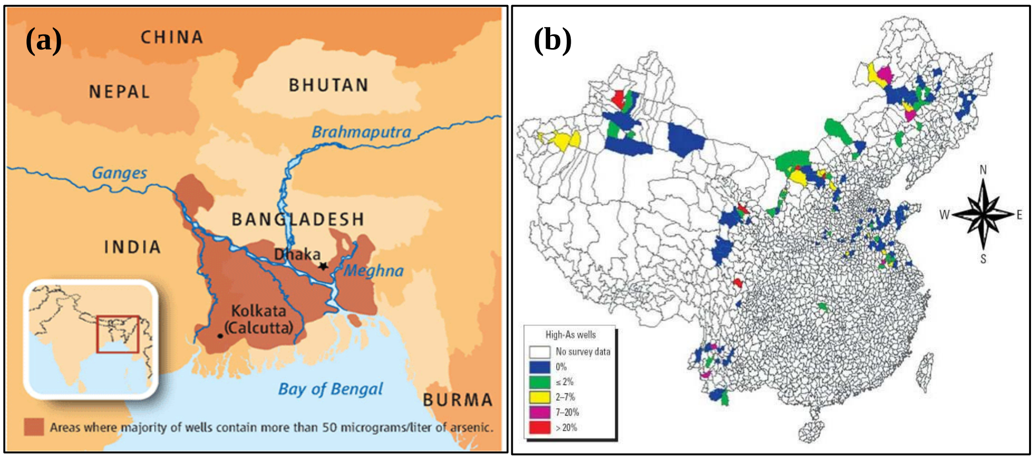

Figure 2.1 (a) Arsenic affected areas around Bay of Bengal in Bangladesh; (b) Percentage of wells containing high concentrations of As at the country level in China as of 2005 [9, 10].

Lead is a chemical element places under group IV A of periodic table, which has an atomic weight of 207.2. The valence of lead is usually (II) rather than (IV). Lead is one of the most commonly used heavy metal in industries and has the ability to become widespread through air, soil, water and food. Among all the heavy metals, lead has been identified as one of the most toxic heavy metals [11]. Lead toxicity could cause mental retardation, anemia, brain damage, and damages to other organs [12]. Children are especially susceptible to chronic lead exposure, with effects including physical, cognitive, and neurobehavioral impairment [13]. Recently, cases of lead poisoning have been increasingly reported in developing countries like China, along with the rapid industrial development and economic growth (Fig. 2.2) [14]. For instance, from 2009 until 2011, lead poisoning in several provinces of China has affected more than 4000 children. In Jiyuan City, Henan Province, blood samples from 1008 of 3108 children (32%) living near lead smelters showed lead concentrations higher than 250 μg/L [15]. Overall, the presence of lead in surface and groundwater with concentrations beyond the permissible limits will bring serious health problems, which should attract more attention on lead emission management as well as remediation of water contamination.

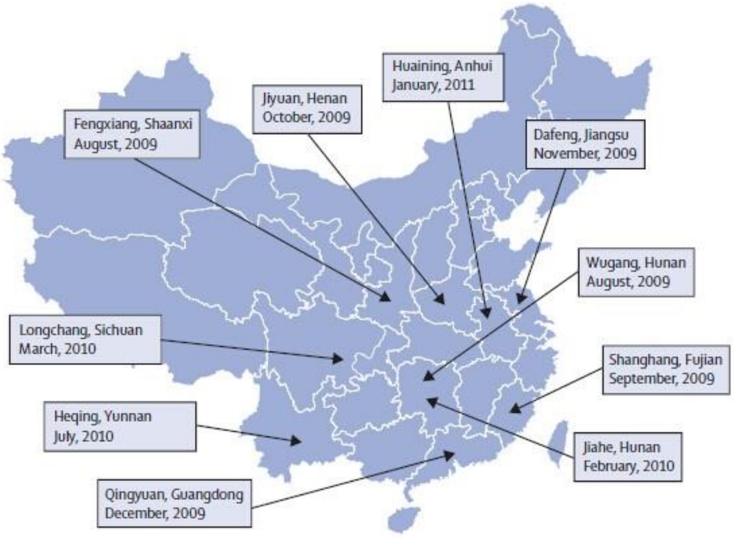

Figure 2.2 Major lead poisoning cases in China since 2009 [15].

2.2 Heavy metal treatment technologies

A variety of techniques including coprecipitation, membrane filtration, iron exchange, reverse osmosis, electrocoagulation, and adsorption have been utilized to remove heavy metal from water [16]. Table 2.1 had listed the comparison of four major heavy metal removal processes, including resource consumption intensity, area required, generated waste and removal efficiency [17]. According to the comparison and practical experience, due to easy operation, cost-effectiveness, and high efficiency, adsorption has been regarded as one of the most promising methods to remove all kinds of heavy metal from water [18]. Many metal oxides such as iron oxide [19], aluminum oxide [20, 21] , manganese oxide [22], titanium oxide [23], and bimetal oxides [24-28] have previously been used to remove arsenic from water, which have also been proved to be applicable for other kinds of heavy metals.

Table 2.1 Comparison of heavy metal removal process [17].

		Precipitation	Membrane	Ion Exchange	Adsorption
Intensity	Chemical	High	Low	Low	Med
	Power	Med	High	Low	Low
	Labor	High	Low	Low	Low
Area Required		High	Low	Low	Low
Waste	Solid	Yes	--	--	--
	Liquid	--	Yes	Yes	Yes
Removal Efficiency		Low	High	High	High

2.3 Application of activated carbon in water treatment

Activated Carbon (AC) is a crude form of graphite with an amorphous structure, which has a well-developed porous, exhibiting a broad range of pore sizes as well as large internal surface area (800 ~ 1000 m^2/g) [29]. It consists of 87 to 97% carbon and such elements as oxygen, hydrogen, sulfur and nitrogen as well as some inorganic components either originating from the raw materials or chemicals used in its production. The use of activated carbon for the water treatment in the United States was first reported in 1930, for the elimination of taste and odor from contaminated water [30]. A wide variety of materials can be used for producing AC, such as wood, coal, bituminous coal, rubber, almond shells, oil-palm stones, polymers, phenolic resins, and rice husks. A variety of activated carbons are available commercially but very few of them are selective for heavy metals and are also very costly[31]. Adsorption of heavy metals on AC are affected by both physical and chemical factors such as the characteristics of the adsorbent (surface area, surface chemistry) and the adsorbate (molecular weight, size, solubility), as well as the background solution conditions (pH, temperature, presence of competitive solutes, ionic strength). Considering the urgent requirement for developing industrially viable, cost-effective, and environmentally compatible technology for the removal of metal ions from wastewater, modified activated carbon has been regarded as one of the promising options. Commercial developed AC has been employed to remediate trivalent and hexavalent chromium from water [32]; AC derived from bagasse was used to adsorb cadmium and zinc [33]; Granular activated carbon (GAC) had also been studied to removal cadmium and lead simultaneously [34]. Nowadays, the depleted source of commercial coal-based AC results in the increase of price. To make progress in heavy metals adsorption to AC without the expense of decline in the pollutants adsorption, additives as well as modifications could be a desirable approach.

2.4 Application of (hydrous) cerium oxide in environmental field

As one of the most abundant and least expensive rare earth metal oxides, cerium oxide and ceria containing materials have been intensively used in metallurgy, catalysis, function ceramic and smart glass materials [35, 36]. It possesses the lowest solubility against acid among the rare earth metal oxides, high specific area and highly assessable adsorption sites, which is believed to be promising alternative adsorbent in removing hazardous anions. For environmental remediation applications, hydrous cerium oxide had demonstrated a high adsorption capacity for hazardous anions, such as bichromate [37], fluoride [38], and arsenate [39]. The mechanism for the adsorption of As(V) to cerium oxide can be explained as follows:

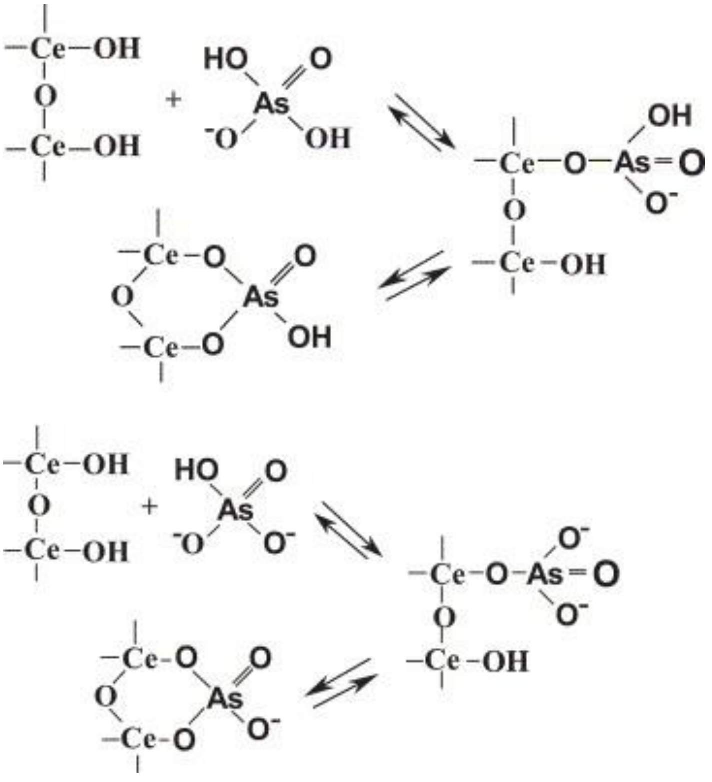

Figure 2.3 The mechanism for the adsorption of As(V) to cerium oxide [39].

According to previous studies, cerium oxide were usually supported on Al_2O_3 [40] and SiO_2 [41], to our best knowledge, there is no research that has reported about AC-based cerium oxide material in the field of heavy metal adsorption. On the other hand, although a good adsorbent for many cations, activated carbon has limited adsorption capacity for anions such as As(III) and As(V) by the limitation of surface group. From this point of view, combine AC with cerium oxide could be a potential approach to generate a kind of multifunctional adsorbent, which might remove both cations and anions simultaneously from aqueous system.

Chapter 3

Materials and methods

3.1 Introduction

Activated carbon and cerium oxide have been widely studied among carbon based adsorbents and metal oxides adsorbents for their extensive applications. For various technical applications, activated carbon is known as an excellent material with large surface area and chemical stability, especially for adsorption remediation. Nanosized (hydrous) cerium oxide is one of the most abundant and least expensive rare earth metal oxides, and has been commonly employed as catalysts, electrolyte materials of solid oxide fuel cells, it is believed to be one of the promising adsorbents in removing hazardous anions.

The present work in this chapter focuses on the fabrication of hydrous cerium oxide and activated carbon with an ease-operated and cost effective approach based on previous studies. The fabricated material was supposed to be a multifunctional adsorbent for both anions and cations, and the emphasis was also on the modification effect as well as preliminary adsorption performance comparing with other two kind of cerium based adsorbents. Scanning Electron Microscopy (SEM) was employed to verify the anchoring of nanosized HCO, while the preliminary adsorption experimental data were analyzed for arsenic concentration by ICP-OES. Method of batch adsorption experiment including adsorption kinetics, isotherms, effects of different factors, as well as models being employed to fit the adsorption experimental data are also elucidated in this chapter.

3.2 Characterization methods and analytical techniques

3.2.1 Scanning Electron Microscopy (SEM)

SEM is a type of electron microscopes that visualize the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern (Fig. 3.1). The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity [42].

The types of signals produced by a SEM include secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays, specimen current and transmitted electrons. BSE are the reflected electrons from the incident beam while the SE is the electron which has escaped from the surface during the bombardment with the incident electrons.[43]

3.2.2 Inductively-Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

ICP-OES is an analytical technique used for the detection of trace metals (Fig. 3.1). It uses inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element [44].

The radiation from excited atoms is unique feature of a specific atom. The concentrations of the elements within the sample are determined by measuring radiation emitted and its intensity from the samples. Argon gas is used to create the plasma during analysis: the argon gas is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the radio frequency (RF) coil. The stable plasma of about 7000 K is then generated as the result of the inelastic collisions created between the neutral argon atoms and the charged particles [45].

Figure 3.1 Picture of SEM (left, JEOL-JSM7600F) and ICP-OES (right, iCAP 7000 Series, Thermo Scientific).

3.3 Materials

3.3.1 Chemicals

As(V), As(III) and Pb(II) stock solutions were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$, $NaAsO_2$ and $Pb(NO_3)_2$ (Sigma–Aldrich, St. Louis, MO, USA) with ultrapure water (resistivity >18.2 MΩ cm) from an integral water purification system (Milli-Q, Millipore, Billerica, MA, USA), respectively, the chemicals were all reagent grade. All other chemicals used in the experiment were of analytical grade, which were also purchased from Sigma-Aldrich Company and used as received without further purification. Humic acid have been previously selected as model humic substances [46-48], hence, it was also employed to represent typical Natural Organic Matter (NOM) in this study. Standard solutions for analytical use were diluted to desired concentrations with ultrapure water. The solution samples after treatment were analyzed for lead concentration by ICP-OES.

3.3.2 Synthesis of materials

Modified particle activated carbon (AC) was first obtained by the following process. 2.5 g granular activated carbon was grinded thoroughly in quartz mortar, then sieved with 45 μm sieve to get micro-size particle activated carbon. Then the particles was immersed into 65% nitric acid. After the mixture was stirred at room temperature (~25 ℃) for 24 h, the particle was separated by centrifugation, and washed with deionized water repeatedly until the supernatant reached neutral pH (7.0). The acquired activated carbon particles were then dried in oven, equally divided into two portions for further modification. Secondly, Cerium Oxide/ethanol solution was prepared according to a two-step process from previous study [49]. Specifically, 0.005 mol $Ce(NO_3)_3$ $6H_2O$ powder was dissolved in 100 mL absolute ethanol in a Duran laboratory bottle, then sonicated for 2 min till the color of solution turned into brown. 0.05 mol NaOH powder was also dissolved in 100 mL absolute ethanol to prepare 0.5 M NaOH/ethanol solution for further use.

After all the above preparation step, take one portion of treated activated carbon to disperse into the 0.05 M Cerium/ethanol solution, agitated with a magnetic agitator under a heating condition of 80 ℃. Then, NaOH/ethanol solution was added dropwisely into the solution under vigorous stirring, until the pH reached around 10. The mixture solution was then dried up and heated in air at 450 ℃ for 1 h. Finally, the precipitation were collected, washed by deionized water and absolute ethanol for several times, and then dried in the oven for 12 h to obtain the nanosized hydrous cerium oxide modified activated carbon (HCO-AC). In order to compare the adsorption performance among different cerium-carbon fabricated materials, we take the other portion of treated particle activated carbon to synthesis cerium oxide modified activated carbon (CO-AC), as well as single hydrous cerium oxide nanoparticles (HCO) in preliminary test, the synthesis process are listed in Table 3.1 as follows.

Table 3.1 Summary of parameters for fabricating HCO-AC, CO-AC and HCO.

Activated Carbon	Cerium Oxide (mol/L)	Hydroxide	Reaction Temperature (℃)	Solvent
1.0 g	0.05	NaOH, pH~10	450	Ethanol
1.0 g	0.05	NaOH, pH~10	450	Milli-Q Water
--	0.1	NaOH, pH~9	25	Ethanol

3.4 Adsorption experiments

3.4.1 Preliminary adsorption experiment

In order to compare the adsorption performance of three cerium based adsorbents, HCO-AC, HCO and CO-AC, which were synthesized from previous experiment, were employed to perform preliminary batch adsorption isotherm experiments for As(V). The adsorptions were carried out by using 3.0 mg of three kind of materials for 30 mL aqueous metal solutions of $Na_2HAsO_4 \cdot 7H_2O$ (Sigma–Aldrich, St. Louis, MO, USA), and the metal solution with adsorbent was put in an orbit shaker under stirring condition to make sure the metal adsorption process reaches the equilibrium. The concentration of As(V) varies from 1 to 20 mg/L. The initial and final concentrations of the metal in the solution were analyzed by ICP-OES. Two measurements were averaged and the equilibrium-sorption capacity (q_e) was calculated from Eqs. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and final arsenic concentrations, respectively. V (L) is the solution volume and m (g) is the mass of adsorbent.

3.4.2 As(V) and As(III) adsorption

Kinetics experiment was first conducted to determine the contact time required to reach adsorption equilibrium. Specifically, 50 mg of adsorbent was dispersed into 500 mL of As(V) or As(III) solution (10 mg/L, pH 5.0) stirred at 220 rpm and 25 ℃ for up to 360 min. An approximately 2 mL aliquot was taken from the suspension and filtered through a 0.45-μm polyethersulfone membrane at designated time intervals. The filtered samples were subsequently analyzed for arsenic concentration.

Adsorption isotherm, effects of solution pH, the influence of competitive anions and NOM on As(V) sorption by the fabricated adsorbents were investigated with batch adsorption experiments at a constant temperature of 25 ℃. 3 mg of HCO-AC was dispersed into 30 mL of As(V) or As(III) solutions with concentration of 10 mg/L in a 50 mL Duran laboratory bottle and sonicated for 1 min. Then the bottles were sealed and stirred in an orbit shaker at 200 rpm for sufficient time to reach adsorption equilibrium. Adsorption isotherms were acquired by varying initial As(V) or As(III) concentrations from 1 to 20 mg/L and the adsorbent dosage of 0.1 g/L at pH 5. Effects of solution pH (from 3 to 9), NOM (humic acid) at the concentrations of 1 to 20 mg/L (as TOC), and competitive anions including sulfate, carbonate and phosphate (1 to 10 mg/L) on the As(V) and As(III) adsorption were also investigated. After reach adsorption equilibrium, the adsorbents were filtered through a 0.45-µm polyethersulfone membrane. The supernatants were analyzed for As concentration by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 7000 Series, Thermo Scientific, MA, Waltham, USA). All batch sorption experiments were performed in duplicate.

3.4.3 Pb(II) adsorption

The forms of metal cations present in solutions were determined by the solution pH. In different pH solutions, divalent metal ions can be in the forms of M^{2+}, $M(OH)^+$, $M(OH)_2^0$, or $M(OH)_3^-$ (M represents for divalent metal ions). At pH ≤ 5, lead ion is present in the form of Pb(II). At pH between 5 ~ 6, $Pb(OH)^+$ can be observed. Further increase of solution pH will induce the precipitation of lead. In order to avoid the effect of lead precipitation, the pH of batch adsorption experiments for Pb(II) was set as 5.0.

In accordance with the arsenic adsorption study, kinetics experiment was also first conducted to determine the contact time required to reach equilibrium. Shaken at 220 rpm under 25 ℃, 50 mg of HCO-AC was dispersed into 500 mL of 10 mg/L Pb(II) solution (initial pH 5.0). Each time, 2 mL of sample was filtered through a 0.45-μm polyethersulfone membrane at desired time intervals. The filtered samples were subsequently analyzed for residual Pb(II) concentration.

In batch adsorption experiments, 3 mg of adsorbent was dispersed into 30 mL of Pb(II) solution contained in a 100-mL Duran laboratory bottle under ultrasonic wave for 1 min. The bottles were shaken at 220 rpm under 25 ℃ in an orbit shaker for sufficient time to reach equilibrium. Effect of solution pH was tested by adjusting the initial solution pH from 3 to 7 with HCl or NaOH. Adsorption isotherm at 25 ℃ was acquired by varying the initial Pb(II) concentrations from 1 to 20 mg/L. For all the rest of the batch experiments, the initial pH of Pb(II) solution was adjusted to 5.0 ± 0.1 with HCl. To investigate the influence of coexisting cations including copper, calcium, magnesium, the corresponding salts were introduced into the Pb(II) solution with concentration from 0 to 20 mg/L. Similarly, humic acid was involved to study the influence of NOM. It is noteworthy that the NOM stock solutions was adjusted to pH 5 with 1 M HCl and then filtered through0.45-μm polyethersulfone membrane prior to use. For each bottle, 5 mL of the supernatant was sampled for ICP-OES analysis. All batch adsorption experiments were performed in duplicate.

3.5 Adsorption kinetic and isotherm models

To better describe the removal efficiency of As(V), As(III) and Pb(II), the adsorption kinetic experimental results were fitted with both Lagergren pseudo-first order kinetic model and the pseudo-second order kinetic model [50], the detail information of these models are listed as follows by Eqs. (2) and (3), respectively.:

$$q = q_{\mathrm{e}}(1 - e^{-k_1 t}) \tag{2}$$

$$q = \left(\frac{1}{q_{\mathrm{e}}} + \frac{1}{k_2 q_{\mathrm{e}}^2} t^{-1} \right)^{-1} \tag{3}$$

where q_{e} and q are the amount of As(V) or As(III) adsorbed (mg/g) at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of adsorption.

The adsorption isotherm of a novel adsorbent is commonly studied by batch adsorption experiment, which can provide crucial information in understanding an adsorption process. The detail information about the three isotherm model are expressed in nonlinear forms as Eqs. (4) [51], (5) [52], and (6) [53], respectively.

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} b c_{\mathrm{e}}}{1 + b c_{\mathrm{e}}} \tag{4}$$

$$q_{\mathrm{e}} = K_{\mathrm{F}} c_{\mathrm{e}}^{1/n} \tag{5}$$

$$q_{\mathrm{e}} = \frac{q_1 b_1 c_{\mathrm{e}}}{1 + b_1 c_{\mathrm{e}}} + \frac{q_2 b_2 c_{\mathrm{e}}}{1 + b_2 c_{\mathrm{e}}} \tag{6}$$

where c_{e} is the equilibrium concentration of arsenic in solution (mg/L), q_{e} is equilibrium adsorption amount (mg/g), q_m is the maximum adsorption amount which signifies the adsorption capacity (mg/g), and b is the Langmuir adsorption constant related to the affinity of binding sites (L/mg). K_F in Eq. (5) is the adsorption affinity coefficient which can be a roughly indicator of the adsorption capacity, n is the heterogeneity factor which has a lower value for more heterogeneous surfaces. q_1 and q_2 in Eq. (6) refer to the maximum adsorption capacity (mg/g) of the low-energy and high-energy adsorption sites on the adsorbent, respectively, while b_1 and b_2 are the affinity coefficients for the both sites in the isotherm (L/mg). The adsorption capacity of the adsorbent is therefore given by the sum of q_1 and q_2 (mg/g).

Chapter 4

Adsorption removal of As(V), As(III) and Pb(II) by HCO-AC

4.1 Introduction

Arsenic and lead has been identified as pollutants of concern by WHO and USEPA, because of their widespread occurrence and toxic, carcinogenic effects to the environment. This chapter reports the removal of As(V), As(III) and Pb(II) from simulated arsenic or lead contaminated aqueous system by adsorption, which is considered as an attractive remediation process, using the fabricated HCO-AC material from the previous experiment. A series of batch adsorption experiment were conducted to study the adsorption performance of the material. The adsorption kinetics as well as isotherms were comprehensively studied through batch adsorption experiment. The effect of solution pH, coexisting anions or cations, existing of NOM were also investigated by varying the concentration of different variables. The solution samples after treatment were analyzed for arsenic concentration by ICP-OES. The mechanism of the adsorption process were further discussed based on the experiment result as well as model fitting.

4.2 Results and discussion of As(V) and As(III) removal

4.2.1 Morphological study of material by SEM

Figure 4.1 showed the SEM images of raw particle activated carbon and nanosized hydrous cerium oxide modified activated carbon. The HCO-AC prepared by the three-step synthesis procedure displays similar morphology and structure compared to raw activated carbon, the particle size was all in micro size scale, which was about 5 ± 1 μm with cubic shape. However, the embedded cluster of nanosized hydrous cerium oxide on the surface of activated carbon could be easily recognized in Fig. 4.1 (right), which are clearly evident for successful fabrication.

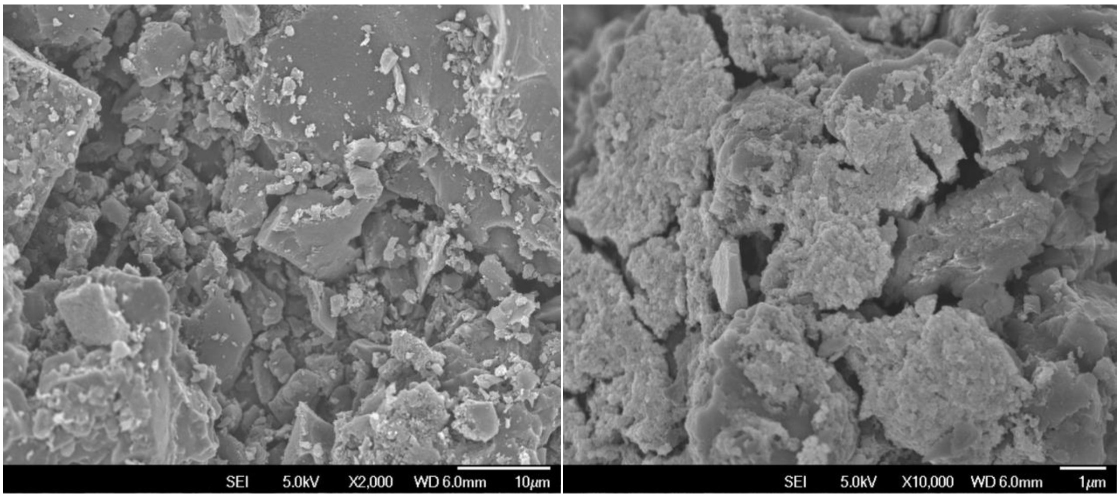

Figure 4.1 SEM images of raw particle activated carbon (left) and nanosized hydrous cerium oxide modified activated carbon (HCO-AC).

4.2.2 Preliminary test of synthesized materials

The experimental data of HCO-AC and other two materials as control group were shown in Fig. 4.2. As can be seen, the adsorption capacity of HCO-AC (44.8 mg/g) had very significant advantage comparing with that of HCO (22.9 mg/g) and CO-AC (13.1 mg/g), which revealed that activated carbon modified by HCO could maximize its adsorption capability for heavy metal anions like arsenic. Therefore, HCO-AC fabricated by the three-step process exhibited remarkable adsorption capacity, which is selected in this study, and the comprehensive adsorption performance of this material as well as its application are described in the following sections.

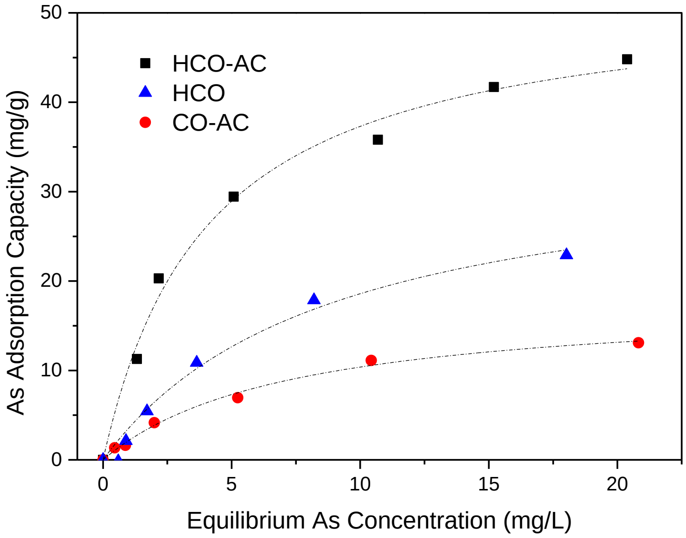

Figure 4.2 Preliminary test of As(V) adsorption isotherms of HCO-AC, HCO and CO-AC at 25 ℃. Dashed line represent Langmuir model fitting. Adsorbent dosage 0.1 g/L; initial solution pH 5.0 ± 0.1.

4.2.3 Adsorption kinetics

In order to model an effective adsorption treatment process, it is important to analyze the rate that heavy metal pollutants are being adsorbed, which further determine the equilibrium time of the whole adsorption process on the solid-liquid interface.

Fig. 4.3 illustrates the kinetics of both As(V) and As(III) adsorption onto HCO-AC at pH 5 with a dosage of 0.1 g/L. It can be seen that for both arsenate and arsenite, the residual concentration rapidly decreased from 10 mg/L to below 7 mg/L within approximately 10 min. After 20 min, the adsorption performance of HCO-AC for both As(V) and As(III) have approached their maximum adsorption capacity, which were larger than 40 mg/g and 30 mg/g, respectively. The adsorption equilibrium for both adsorbents could be obtained in 2 h.

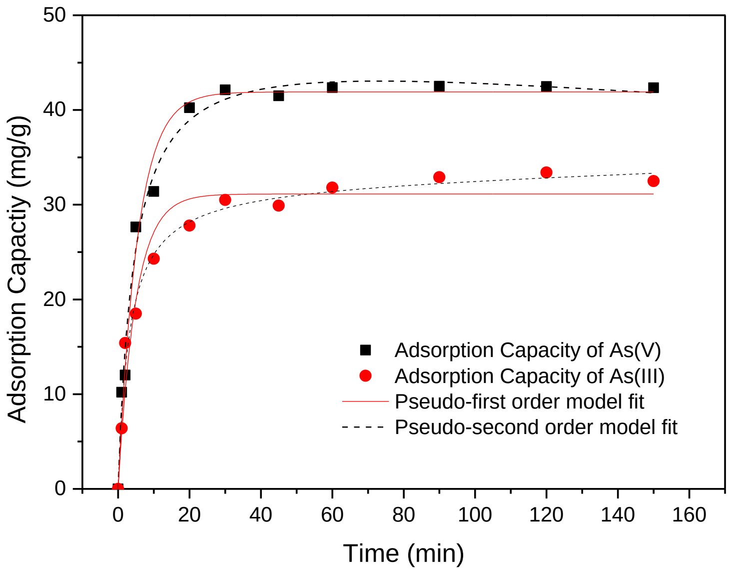

Figure 4.3 As(V) and As(III) adsorption kinetics of HCO-AC at 25 ℃. Solid line and dashed line represent Lagergren pseudo-first order kinetic model and the pseudo-second order kinetic model fitting, respectively. Adsorbent dosage 0.1 g/L; initial solution pH 5.0 ±0.1.

As can be seen from the fitting results in Table 4.1, even though the pseudo-first order model could also generally fit the kinetics of both arsenate and arsenite adsorption by HCO-AC ($r^2 > 0.95$), the pseudo-second order kinetic model could more accurately describe the adsorption removal process for both arsenic oxyanions with the coefficients of determination (r^2) greater than 0.99. This observation suggested that a chemical sorption involving valence forces through sharing or exchange of electrons between arsenic and the adsorbents might be the rate limiting step of As(V) and As(III) adsorption [54]. Similar result has also been previously found for the adsorption of As(V) and As(III) on hierarchically porous CeO_2-ZrO_2 nanospheres [55], as well as La(III) and Ce(III) loaded Orange Waste Gels [56].

Table 4.1 Summary of adsorption kinetics fitting data for As(V) and As(III) adsorption on HCO-AC at 25 ℃. Initial arsenic concentration 10 mg/L, adsorbent dosage 0.1 g/L, initial solution pH 5.0 ± 0.1.

Adsorbate	q_e(exp) (mg/g)	pseudo-first order model			pseudo-second order model		
		k_1 (min^{-1})	q_e(cal) (mg/g)	r^2	k_2 (g mg^{-1} min^{-1})	q_e(cal) (mg/g)	r^2
As(V)	42.51	0.017	12.83	0.9848	0.0097	43.29	0.9992
As(III)	32.90	0.020	12.76	0.9560	0.0094	33.56	0.9989

4.2.4 Adsorption isotherms

Adsorption isotherms of HCO-AC for both As(V) and As(III) at pH 5 were investigated and the corresponding results were provided in Fig. 4.4. The experimental data of the material for both adsorbates were analyzed with classic adsorption isotherm models including Langmuir, Freundlich, and two-site Langmuir models.

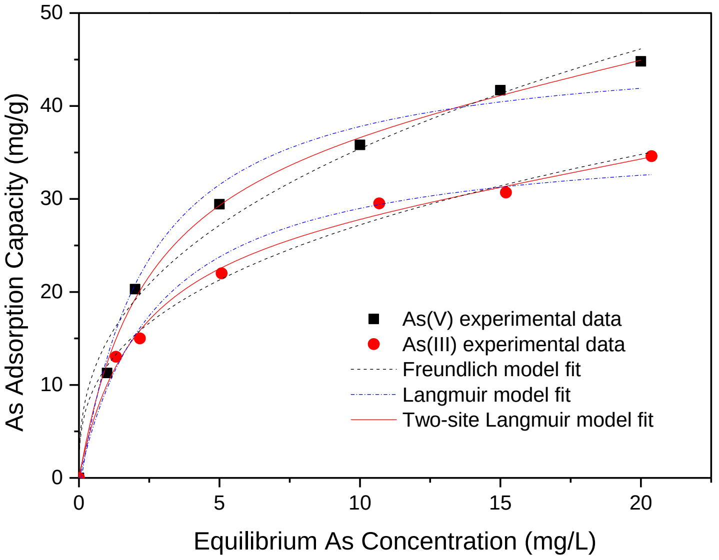

Figure 4.4 As(V) and As(III) adsorption isotherms of HCO-AC at 25 ℃. Dash line, Dash-Dot line and solid line represent Freundlich model fitting, Langmuir model fitting and two-site Langmuir model fitting, respectively. Adsorbent dosage 0.1 g/L; initial solution pH 5.0 ± 0.1.

The parameters derived from above model fitting were provided in Table 4.2. Both Langmuir and Freundlich isotherm could generally capture the trend of experimental data, the r^2 of which were both above 0.96. Comparing the coefficients of determination (r^2) for all these three isotherms, two-site Langmuir model could fit the experimental result best (As(V), r^2 = 0.9989; As(III), r^2 = 0.9992). The total adsorption capacity of HCO-AC for As(V) and As(III) at pH 5 and 25 ℃ yielded by two-site Langmuir model were found to be the sum of q_1 and q_2, which were 46.18 mg/g and 36.93 mg/g, respectively.

Table 4.2 Summary of isotherm fitting for adsorption of As(V) and As(III) on

HCO-AC at 25 ℃. Adsorption dosage 0.1g/L, initial pH 5.0 ±0.1.

Model	Parameter	As(V)	As(III)
Langmuir (non-linear)	q_m (mg/g)	44.64	34.25
	b (L/mg)	1.738	1.359
	r^2	0.9960	0.9909
Freundlich (non-linear)	k	1.362	0.6890
	n	27.10	43.67
	r^2	0.9697	0.9847
Two-site Langmuir	q_1 (mg/g)	45.15	33.87
	q_2 (mg/g)	1.032	3.063
	b_1 (L/mg)	472.6	378.5
	b_2 (L/mg)	0.983	1.041
	r^2	0.9989	0.9992

Besides, both of the As(V) and As(III) adsorption capacities of HCO-AC are larger than those of other carbon and metal based adsorbents reported in previous studies shown in Table 4.3, even in the condition of lower initial As(V) and As(III) concentration. The above result clearly indicated that HCO-AC have a large As(V) adsorption capacity, and the combination of nanoscale hydrous cerium oxide with activated carbon could significantly enhance the adsorption capacity for As(V) as well as As(III).

Table 4.3 Comparison of As(V) and As(III) adsorption capacity of HCO-AC with those of other carbon and metal based adsorbents reported in previous studies.

Adsorbents	Initial Conc. (mg/L)	Initial pH	Adsorption Capacity (mg/g)		References
			As(V)	As(III)	
Magnetic iron oxide @carbon encapsulates	15.0	7.0	17.9	29.4	[57]
Polyaluminum granulate	22.5	7.5	14.85	18.0	[58]
CeO_2-ZrO_2 hollow nanospheres	60	6.7-7.1	27.1	9.2	[55]
GAC-Fe-NaClO	10	4.7	6.57	n.a.	[59]
Soot carbon (AC)	7-10	6.9-7.5	13.3	29.92	[60]
HCO-AC	20	5.0	46.18	36.93	This study

4.2.5 Effect of solution pH

The distribution of both arsenate and arsenite species in aqueous system as well as the surface property of adsorbent are highly pH-dependent. It is expected that by adjusting solution pH, the adsorption capacity of novel synthesized material could be optimized. The effects of solution pH (from 3 to 9) on the removal of As(V) and As(III) by HCO-AC were investigated and the results were presented in Fig. 4.5. As can be seen from the figure, for arsenate, the adsorption capacity maintained a high level which was over 25 mg/g in a broad pH range from 3 to 6. For arsenite, the adsorption capacity was also higher than 25 mg/g in the pH range of 4 to 7. The fabricated material could reach maximum adsorption capacity at pH 5 for both As(V) and As(III), which were in accordance with the previous kinetic and isotherm studies. Under alkaline pH condition, the adsorption performance of HCO-AC for both As(V) and A(III) had a significant decline, however, even in pH range from 7 to 9, the adsorption capacity for As(V) and As(III) were still larger than 5 mg/g and 10 mg/g, respectively, which indicated that HCO-AC was able to be utilized in a wide pH range by varying dosage, and the adsorption performance for As(III) could be more stable comparing with that of As(V).

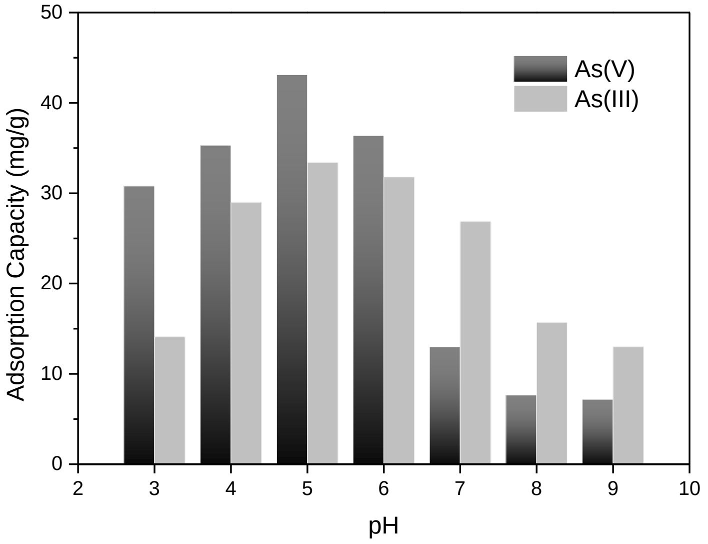

Figure 4.5 Effect of initial solution pH on As(V) and As(III) removal by HCO-AC. Initial As(V) and As(III) concentration 10 mg/L; adsorbent dosage 0.1 g/L; temperature 25 ℃.

4.2.6 Effect of coexisting anions

A variety of anions widely exist in natural water system including surface and ground water. According to real water condition, the effect of three commonly coexisting anions in aquatic environment including sulfate, bicarbonate and phosphate on the adsorption of As(V) and As(III) by HCO-AC were investigated in a wide anion concentration from 1 to 10 mg/L, and the corresponding results were shown in Fig. 4.6. As can be seen from the figure, the presence of all the three anions including sulfate, bicarbonate and phosphate could decrease the adsorption performance of both As(V) and As(III) by HCO-AC, which is in accordance with our expectation. Specifically, the increasing concentration of sulfate and bicarbonate (from 1 to 10 mg/L) deceased the adsorption capacity for As(V) from 31.26 mg/g and 38.38 mg/g to 23.9 mg/g and 21.1 mg/g, respectively, while the competitive effects of the two anions caused the adsorption capacity for As(III) slightly decreased from 39.62 mg/g and 34.19 mg/g to 36.63 mg/g and 29.55 mg/g, respectively, which were even more negligible than that of As(V). It can be concluded that even when the two coexisting anions were at the concentration of 10 mg/L, the adsorption performance could still maintain a high level of capacity which were larger than 20 mg/g. The observation indicated that HCO-AC was able to remove As(V) and As(III) in the presence of up to 10 mg/L of sulfate and bicarbonate. On the other hand, the coexisting of phosphate have a significant negative impact on arsenic removal due to their extraordinary similarity of chemical properties, according to the experimental result. The adsorption capacity for As(V) and As(III) dropped from 32.4 mg/g and 36.69 mg/g to 9.0 mg/g and 13.1 mg/g, respectively, which were larger than 50% of the maximum adsorption capacity.

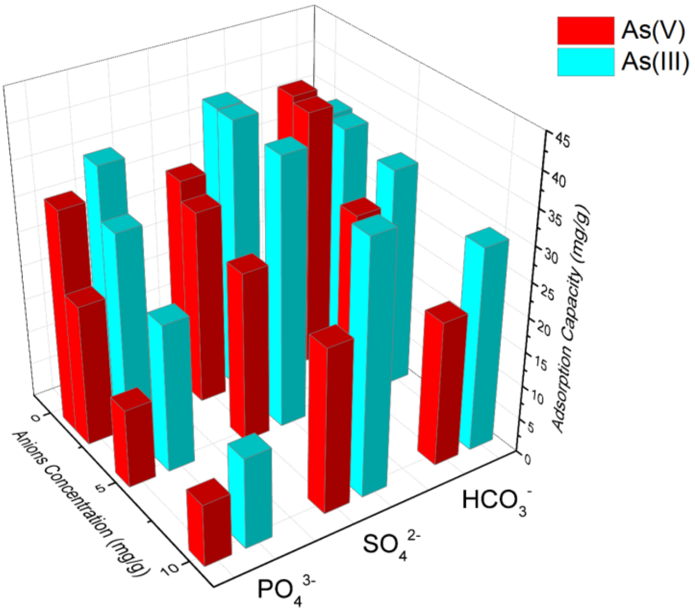

Figure 4.6 Effect of coexisting anions on As(V) and As(III) adsorption performance by HCO-AC. Initial As(V) and As(III) concentration 10 mg/L; adsorbent dosage 0.1 g/L; initial solution pH 5.0 ± 0.1; temperature 25 ℃.

The insignificant influence of both sulfate and bicarbonate have been reported previously [61-63]. The effects of sulfate and bicarbonate on the removal of As(V) observed for both types of fabricated materials were all within anticipation according to their bonding interaction. Sulfate would be absorbed predominantly via outer-sphere complexation at around pH 6 [64, 65]. However, through the mechanism of ligand exchange, arsenic oxyanions could form much more firmly bonded inner-sphere complex with the adsorbent. Thereby, even though the concentration of sulfate reached 10 mg/L which was same to that of arsenic oxyanion, the removal of As(V) by HCO-AC were not obviously affected by sulfate. The shared charge theory [66] could explain the preference for arsenate over (bi)carbonate with the fact that the shared charge of arsenate (1.25) is smaller than that of (bi)carbonate (1.33). Furthermore, despite that both anions could form inner-sphere complex, affinity of carbonate was relatively weaker than arsenate [62]. As a result, (bi)carbonate did not obviously affect the adsorption of As(V).

Previous studies have shown that the decline of arsenic removal capacity in the presence of phosphate could due to competitive adsorption. For example, Chowdhury and Yanful [67] found that the adsorption percentage of total arsenic onto magnetite-maghemite nanoparticles decreased to ~30% when 10 mg/L of phosphate was co-present in solutions, Zhang et al. [68] reported that the presence of 6.5 mg/L phosphate reduced As(V) adsorption capacity of iron core at pH 7 by 30-50%. Moreover, the adsorption capacity of HCO-AC was higher than 30 mg/g at phosphate concentration of 1 mg/L, which was the typical concentration of phosphate widely found in natural water system. If phosphate with high concentration was presented in water system, high adsorption capacity of arsenic could still be achieved by simply increasing the dosage of adsorbents.

4.2.7 Effect of natural organic matter

The influence of NOM, present ubiquitously in the aquatic environment with typical concentrations from 1 to 20 mg/L, on the adsorption of As(V) and As(III) was also investigated, and the results were presented in Fig. 4.7. Humic acid from 1 to 20 mg/L were used to model humic substance, which is the major components of NOM. As can be seen from the figure, the increase of humic acid concentration in solutions slightly decreased the uptake of As(V) and As(III) by HCO-AC. The decrease in As(V) adsorption induced by humic acid was relatively greater than As(III), which was from 36.69 mg/g to 21.26 mg/g, while the decline of As(III) adsorption capacity was from 30.47 mg/g to 25.48 mg/g. However, even in the humic acid concentration of 20 mg/L, the corresponding adsorption capacity of HCO-AC for both oxyanions were still larger than 20 mg/g.

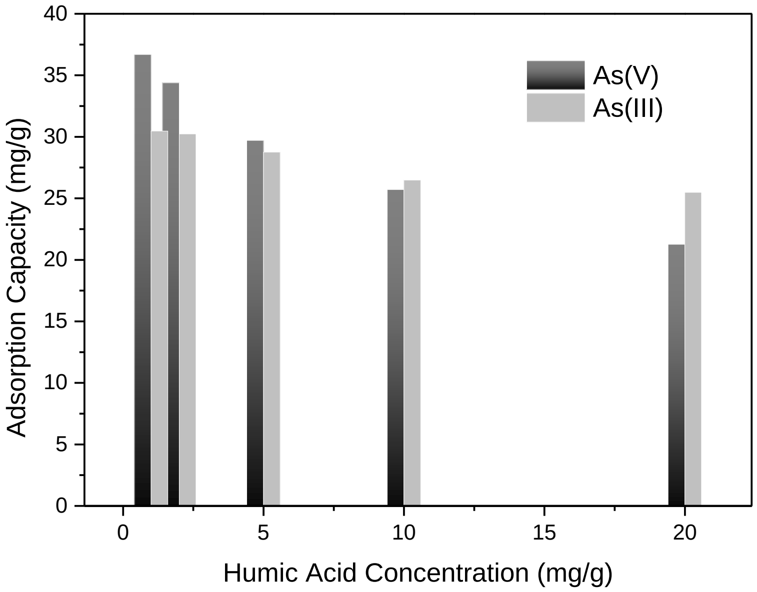

Figure 4.7 Effect of humic acid on As(V) and As(III) removal by HCO-AC. Initial arsenic concentration 10 mg/L; adsorbent dosage 0.1 g/L; initial solution pH 5.0 ± 0.1; temperature 25 ℃.

The decrease in arsenic adsorption efficiency with increasing humic acid concentration has also been previously observed [52]. The negatively charged humic acid could compete with $H_2AsO_4^-$, $HAsO_4^{2-}$, $H_2AsO_3^-$ and $HAsO_3^{2-}$, the dominant species of As(V) and As(III) in a wide pH range, for adsorption sites on material surfaces. The above observation indicated that the novel HCO-AC material fabricated in our study could be effective adsorbents for As(V) and As(III) removal in the presence of NOM.

4.3 Results and discussion of Pb(II) removal

4.3.1 Adsorption kinetics

Fig. 4.8 illustrates the kinetics of Pb(II) adsorption onto HCO-AC at pH 5 with a dosage of 0.1 g/L. The residual concentration rapidly declined from 10.34 mg/L to 6.88 mg/L within approximately 20 min. After 30 min, the adsorption capacity of HCO-AC for Pb(II) have approached their maximum, which were larger than 40 mg/g. The adsorption equilibrium could be obtained in 2 h.

To further analyze the removal of Pb(II), the adsorption kinetic experimental data were also fitted with both Lagergren pseudo-first order kinetic model and the pseudo-second order kinetic model, the detail information of these models could be found in chapter 3.

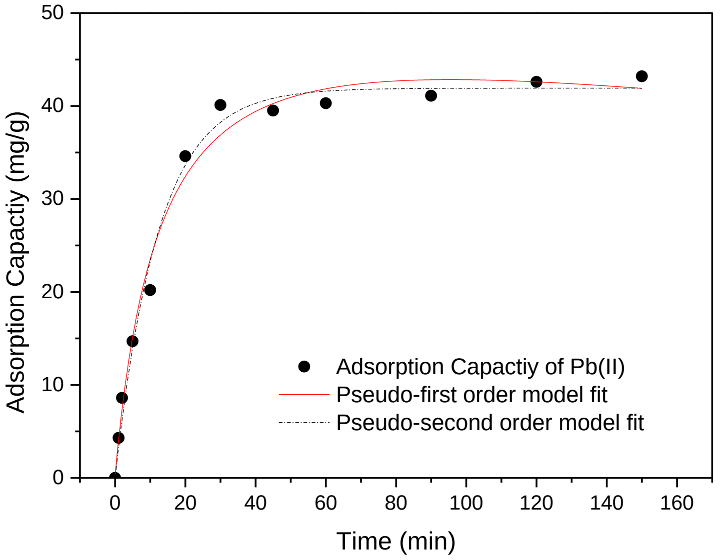

Figure 4.8 Pb(II) adsorption kinetics of HCO-AC at 25 ℃. Solid line and dashed line represent Lagergren pseudo-first order kinetic model and the pseudo-second order kinetic model fitting, respectively. Adsorbent dosage 0.1 g/L; initial solution pH 5.0 ± 0.1.

According to the fitting results in Table 4.4, the pseudo-second order kinetic model could more accurately describe the adsorption process ($r^2 > 0.99$) rather than the pseudo-first order model ($r^2 > 0.98$). Similar to the kinetics of arsenic adsorption, This observation suggested that chemical sorption involving valence forces were the rate limiting step of Pb(II) adsorption as well. Previous Studies have also reported the similar result which employing activated carbon [69], activated alumina [70] and lichen biomass [71] and to adsorb Pb(II) in aqueous systems.

Table 4.4 Summary of adsorption kinetics fitting data for Pb(II) adsorption on HCO-AC at 25 ℃. Initial lead concentration 10 mg/L, adsorbent dosage 0.1 g/L, initial solution pH 5.0 ±0.1.

Adsorbate	q_e(exp) (mg/g)	pseudo-first order model			pseudo-second order model		
		k_1 (min^{-1})	q_e(cal) (mg/g)	r^2	k_2 (g mg^{-1} min^{-1})	q_e(cal) (mg/g)	r^2
Pb(II)	43.20	0.033	24.72	0.9840	0.0025	45.45	0.9902

4.3.2 Adsorption isotherms

Adsorption isotherms of HCO-AC for Pb(II) at pH 5 were investigated and the corresponding results were provided in Fig. 4.9. The experimental data of the material for both adsorbates were analyzed with classic adsorption isotherm models including Langmuir, Freundlich, and two-site Langmuir models. The detail information about the three model were listed in section 3.3.4.

The parameters derived from above model fitting were provided in Table 4.5. Langmuir model could generally describe the trend of experimental data rather than Freundlich isotherm, the r^2 of which were 0.99 and 0.94, respectively. Comparing the coefficients of determination (r^2) for Langmuir and two-site Langmuir isotherm models, two-site Langmuir model could fit the experimental result even better (r^2 = 0.9977).

Table 4.5 Summary of isotherm fitting for adsorption of Pb(II) on HCO-AC at 25 ℃. Adsorption dosage 0.1g/L, initial pH 5.0 ±0.1.

Model	Parameter	Pb(II)
Langmuir (non-linear)	q_m (mg/g)	45.45
	b (L/mg)	1.582
	r^2	0.9939
Freundlich (non-linear)	k	0.4674
	n	10.66
	r^2	0.9424
Two-site Langmuir	q_1 (mg/g)	46.75
	q_2 (mg/g)	1.77
	b_1 (L/mg)	327.4
	b_2 (L/mg)	0.860
	r^2	0.9977

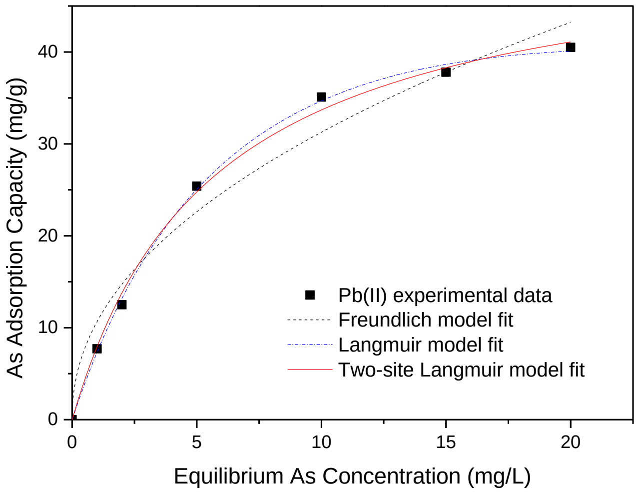

Figure 4.9 Pb(II) adsorption isotherms of HCO-AC at 25 ℃. Dash line, Dash-Dot line and solid line represent Freundlich model fitting, Langmuir model fitting and two-site Langmuir model fitting, respectively. Adsorbent dosage 0.1 g/L; initial solution pH 5.0 ±0.1.

The total adsorption capacity of HCO-AC for Pb(II) at pH 5 and 25 ℃ yielded by two-site Langmuir model was found to be the sum of q_1 and q_2, which was 48.52 mg/g. The observation suggested that despite the large adsorption capacity for arsenic, HCO-AC could also act as an effective lead removal adsorbent, the combination of nanoscale hydrous cerium oxide with activated carbon could generate a kind of multifunctional cations and anions adsorbent.

4.3.3 Effect of solution pH

In the pH range of 5 ~ 6, $Pb(OH)^+$ will be observed in aqueous system. Excessive hydroxyl ion will induce the significant precipitation of lead under alkali pH condition, therefore, in order to avoid the effect of lead precipitation, batch adsorption experiment for pH effect was set in the pH range of 3 to 6. Fig. 4.10 showed the adsorption of Pb(II) onto HCO-AC as a function of pH. The metal uptake increases from a lower pH and reaches a plateau at equilibrium pH 6, the adsorption capacity could be 7 times (31.71 mg/g) as much as the capacity under pH 3 (4.5 mg/g). The adsorption of other metal ions such as copper also demonstrated a similar behavior[72]. Nevertheless, the final pH of solution after adsorption might significantly increase, thus, in order to avoid precipitation, pH 5 was selected as the adsorption condition, which was corresponding to that of arsenic adsorption. The study also indicated that HCO-AC was able to achieve best adsorption performance in neutral pH range, the improvement of adsorption capacity could also be obtained by varying dosage.

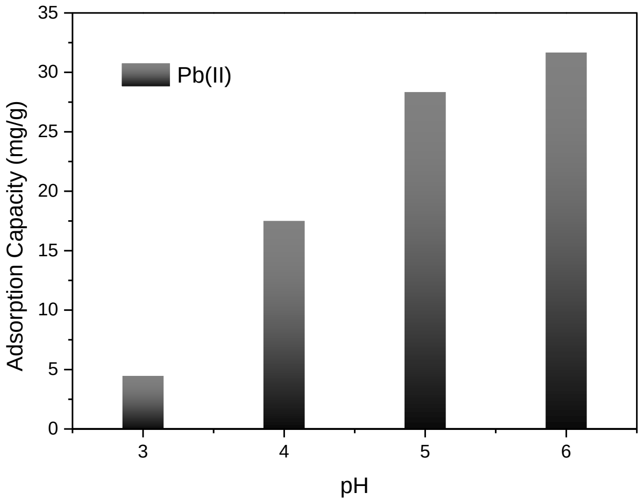

Figure 4.10 Effect of initial solution pH on Pb(II) removal by HCO-AC. Initial Pb(II) concentration 10 mg/L; adsorbent dosage 0.1 g/L; temperature 25 ℃.

4.3.4 Effect of coexisting cations

According to real water condition, the effect of two commonly coexisting cations in aquatic environment including calcium and magnesium, as well as another widely existed heavy metal in contaminated water, copper, were investigated on the adsorption of Pb(II) by HCO-AC in a wide cation concentration from 1 to 20 mg/L, and the corresponding results were shown in Fig. 4.11. As can be seen from figure (a), none of the two coexisting cations had obvious effect on the uptake of Pb(II) by HCO-AC even at a very high concentration of 20 mg/L, the adsorption capacity of material slightly decreased from 38.57 mg/g and 37.02 mg/g to 32.43 mg/g and 31.01 mg/g, respectively, which indicated that the adsorption performance of the material under both condition could still maintain a high level of capacity which were larger than 30 mg/g.

On the other hand, The existence of copper led to a significant improvement in Pb(II) adsorption on HCO-AC, the capacity increased from 20.6 to 134.75 mg/g with the increasing of copper concentration. The non-competitive influence observed for Cu(II) on Pb(II) adsorption could be due to the greater atomic weight and electronegativity of the later metal [73]. The observed reduction in the sorption of Cu(II) and Zn(II) in the presence of Pb(II) could be attributed to the difference in their class behavior on the basis of their covalent indices [74]. Pb(II) is classified as a class b ion, while Cu(II) are classified as borderline ions. Since Pb(II) belongs to a different class of ions, other cations do not exert any effect on its sorption. On the basis of this argument, it is possible to explain the competition effects observed in the present study. However, the possibility of precipitation should be entirely excluded in further study, and more detailed explanation to the mechanism still need further experiment research.

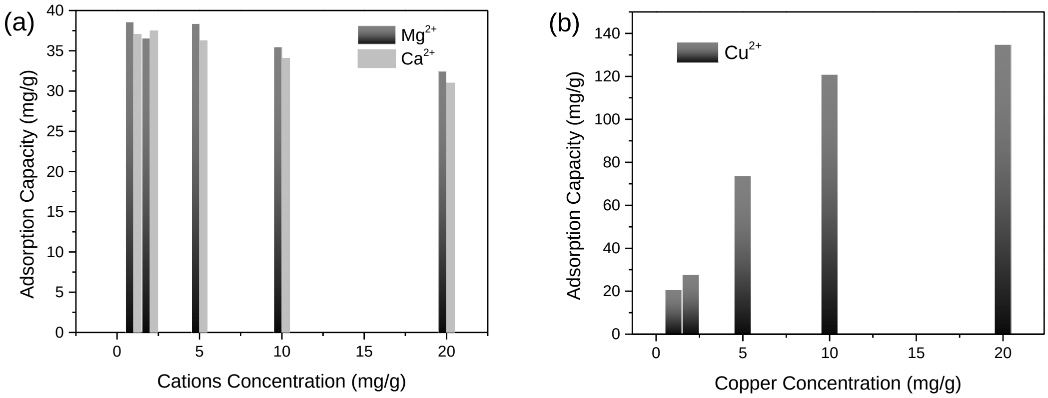

Figure 4.11 Effect of calcium and magnesium (a) and copper (b) on Pb(II) adsorption performance by HCO-AC. Initial Pb(II) concentration 20 mg/L; adsorbent dosage 0.1 g/L; initial solution pH 5.0 ±0.1; temperature 25 ℃.

4.3.5 Effect of natural organic matter

Humic acid from 1 to 20 mg/L were used to model humic substance, which is the major components of NOM. Fig. 4.12 showed that the increase of humic acid concentration in solutions significantly increased the uptake of Pb(II) by HCO-AC, The adsorption capacity improved from 29.48 mg/g to 87.31 mg/g, which indicated that instead of causing negative impact on Pb(II) removal by HCO-AC, the existing of NOM could even improve the adsorption performance of the material in solution.

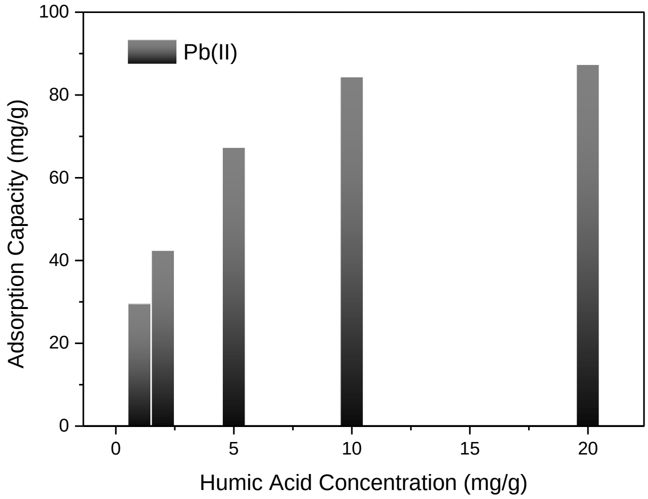

Figure 4.12 Effect of humic acid on As(V) and As(III) removal by HCO-AC. Initial arsenic concentration 20 mg/L; adsorbent dosage 0.1 g/L; initial solution pH 5.0 ±0.1; temperature 25 ℃.

The mechanism could be explained as follows. The chemical interaction between the metal ions and the surface functional groups of carbon has been reported to contribute the adsorption of metal ions on carbon [75, 76]. Previous studies [77, 78] have also shown that functional groups such as carboxyl, carbonyl, and hydroxyl appeared on the surface of carbon after oxidation pretreatment could improve the adsorption capacities of Pb(II). Accordingly, the addition of NOM in the solutions induced negative zeta potentials on the surface of the material, which indicated the adsorption of NOM on the surfaces of HCO-AC would cause zeta potentials of the material to be negative. Furthermore, the major functional groups in NOM has been found to be carboxyl and phenolic groups [79], the amount of these functional groups on the surfaces of HCO-AC would be higher depending on the concentration of NOM, which could interact with Pb(II) by chemical bonding, therefore the adsorption capacity for Pb(II) of the material was observed to be higher with the presence of NOM in solutions. This results in our study indicated that the synthesized HCO-AC could be utilized as a good adsorbent for Pb(II) removal from water containing NOM (humic acid) with concentration up to 20 mg/L.

Chapter 5

Conclusions and recommendations

5.1 Concluding remarks

In this study, nanosized hydrous cerium oxide was successfully loaded on the surface of particle activated carbon to obtain a kind of novel adsorbent, HCO-AC, with an easy-operated and cost effective approach. Comparing with that of single hydrous cerium oxide as well as cerium oxide modified activated carbon, the modification significantly improved the adsorption performance of arsenic, the total adsorption capacity of HCO-AC for As(V) and As(III) at pH 5 and 25 ℃ were increased to 46.18 mg/g and 36.93 mg/g, respectively, both of which were also larger than some other materials been reported in previous studies. Furthermore, the fabricated material also have a notable adsorption performance for Pb(II) removal, the adsorption capacity of which could also reach 48.52 mg/g. The adsorption kinetics of HCO-AC for all of As(V), As(III) and Pb(II) could be well described by pseudo-second order model. Two-site Langmuir isotherm model derived from classic Langmuir model could more accurately fit the adsorption isotherm of all the adsorption process for arsenic and lead. HCO-AC could be utilized for efficient As(V) and As(III) removal in a wide pH range from 3 to 6 and 4 to 7, respectively, or be utilized as a kind of large adsorption capacity adsorbent for Pb(II) removal in slight acid pH condition from 5 to 6. The presence of selected commonly coexisting anions or cations did not have significant influence on the adsorption capacity of HCO-AC for arsenic and lead, despite the coexisting of phosphate and copper could lead to obvious decreasing and increasing to the adsorption capacity of the material, respectively. Even in this case, high removal efficiency of arsenic onto the material could still be obtained by adjusting dosage into the solutions. As a compound of organic groups, the presence of NOM in aqueous system could compete with arsenic adsorption, as well as improving the adsorption capacities of Pb(II), because of the negative zeta potentials induced by the organic groups from NOM onto the surface of the material. Therefore, the HCO-AC synthesized in this study can serve as a multifunctional, promising and highly efficient adsorbent for simultaneously removal of As(V), As(III) and Pb(II) from aqueous environment.

5.2 Recommendations

1. Various of characterization approach including XRD, XPS, Raman Spectroscopy are recommended to be conducted for further characterization of the fabricated HCO-AC for its surface structure and area, the formation of chemical bonds between cerium oxide, activated carbon and target ions, as well as the mechanism of competitive adsorption between target ions and other coexisting ions in water, which could reveal more details about the adsorption behavior of the material, so as to further optimize the synthesis process of HCO-AC and achieve better multifunctional adsorption performance.

2. Real waters are more complicated relative to the synthetic aqueous system. For instance, the existence of organic matters, various kinds of salts, and even microbes

may influence the adsorption of arsenic and lead. Taking these factors into account, it would be interesting to investigate the adsorption behavior of the novel material in real water like tap water, lake water or groundwater, to verify that whether HCO-AC could also perform as highly effective adsorbent in natural circumstance for the removal of all the three kind of heavy metal pollutants.

3. It would be important to explore other nanosized metal oxide such as activated alumina, magnetic nanoparticles, or some other lanthanide metal oxide to be used as chemical modifications to anchor onto different carbon-base material, for example, multiwall carbon nanotube (MWCNT) and carbon fiber, then the adsorption performance of the fabricated candidates also can be comprehensively examined to verify their multifunctional capability in aqueous system for not only arsenic and lead, but other commonly existed heavy metals, which may provide more options for the adsorption remediation of multiple heavy metal polluted water.

References

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