Study of arsenic(V) adsorption on bone char from aqueous solution

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ABSTRACT

Arsenic is a toxic element and may be found in natural waters as well as in industrial waters. Leaching of arsenic from industrial wastewater into groundwater may cause significant contamination, which requires proper treatment before its use as drinking water. The present study described the removal of As(V) on bone char in batch studies conducted as a function of pH, dosage of adsorbent, and contact time. Kinetics revealed that uptake of As(V) ion by bone char was very rapid in the first 30 min and equilibrium time was independent of initial As(V) concentration. And the adsorption process followed a first-order kinetics equation. The arsenic removal was strongly dependent on pH and dosage of adsorbent. Fourier transform infrared spectra of bone char before and after As(V) adsorption demonstrated that Ca–OH functional group plays an important role for As(V) ions removal, and the mechanisms of the removal of As(V) on bone char was complex mechanism where both co-precipitation and ion exchange. The results suggested that bone char can be used effectively for the removal of As(V) ion from aqueous solution.

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1. Introduction

Human poisoning and death from arsenic have occurred as a result of drinking water contaminated with arsenic in Bangladesh [1], India [2] and other countries of the world. Chronic arsenism poses a serious health problem in China also. About 14.6 million people, who are mainly distributed in the northwest China including Inner Mongolia, Xinjiang, are exposed to drinking water containing arsenic with a concentration of 0.03 mg l^{-1} or higher [3]. If Chinese current drinking water standard of As lowers from 0.05 to 0.01 mg l^{-1}, a level adopted by WHO [4] and some industrialized countries [5], the population affected will decrease significantly. It is of great importance to develop alternative technologies for treating drinking water contaminated with arsenic effectively at a reasonable cost.

Various technologies such as ion exchange, adsorption [6] and coagulation [7] have been employed for arsenic removal from water. Compared with aluminum coagulants, iron(III) salts have been found to be more effective for arsenic removal [8]. Although the coagulation process is a simple and economical way, it produces a wet bulky sludge, and furthermore, could not satisfy the stringent standard of WHO. Because of the ease of handling, sludge-free oper-

ation, and by using acid or base leaching to regenerate the sorbent bed, the adsorption process appears to be the most promising one.

Activated carbon has traditionally been the most widely used as adsorbent for many organic compounds and metal ions [9,10]. According to Liu [11], the removal of chromium(VI) has been studied using modified carbon. However, activated carbon is a relatively expensive adsorbent and may not work well for arsenic systems [12]. In recent years, many low-cost sorbents including agricultural waste and byproducts have also been tested in batch and fixed bed sorption systems by a number of authors. For example, peanut husks to remove metal ions from wastewaters [13], corn-cob fragments to remove cadmium [14], coir pith to adsorb procion orange from wastewater [15]. Coconut copra meal have been used for cadmium sorption from water [16], and human hair has been tested for the sorption of lead, aluminum and cadmium [17]. The ability of bone char to adsorb considerable quantities of metal ions has been demonstrated recently [18,19].

Bone char is derived from the carbonization of the crushed animal bones by heating them to 500–700 °C in an airtight iron retort for 4–6 h. The crushed bone, after the heating process, will form the bone charcoal which is composed of calcium hydroxylapatite (CaHAP) (70–76 wt%), carbon content (9–11 wt%), calcium carbonate (7–9 wt%), etc. Bone char has been used extensively as an adsorbent for the decolorization of cane sugar [20]. This sorbent was used as the defluoridating agent at the Shanxi, China [21]. However, bone char as an adsorbent to remove arsenic ions has been seldom reported.

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In this research, the sorption of arsenic(V) onto bone char in an agitated batch sorber has been studied. The objective of the present work is to assess the function of pH, contact time, adsorbent dosage, and initial arsenic concentration on the As sorption onto bone char.

2. Materials and methods

All reagents were of analytical grade. A stock solution of As(III) made by using double-distilled water, and arsenic-silver diethyldithiocarbamate were used for arsenic determination [22]. Standard acid ($0.5\,M\,H_2SO_4$) and calcium hydroxide saturated solution were used for pH adjustments.

pH measurements were made by a pH meter, Model pHS-3 C, Leici-Shanghai, China. Arsenic determination was carried out with arsine generator, and later with spectrophotometer, Model VIS-7220 at a wavelength of 530 nm.

2.1. Absorbates: As(V) ion

Sodium arsenate ($Na_3AsO_4{\cdot}12H_2O$) was used as the source of As(V). A stock solution ($1000\,mg\,l^{-1}$) was prepared in 1000 ml distilled water by dissolving 5.6583 g of sodium arsenate. As(V)-bearing water was prepared by diluting As(V) stock solution to given As concentrations with tap water.

2.2. Absorbent: bone char

The bone char used in this study was supplied by a Biochemistry Ltd., Sichuang, China. The physical and chemical properties of bone char were provided by the manufacturer. Table 1 shows that the main composition of bone char is CaHAP. The carbon is distributed throughout a porous structure of hydroxyapatite in the bone char.

Bone char was directly used without sieved because the percentage of 500–710 μm particle size is some 90%.

2.3. Experiment methods

Batch sorption experiments were conducted to obtain equilibrium data, using 1000 ml Bunsen beaker kept at room temperature; a magnetic stirrer was used to agitate the solution. The reaction mixture consisted of 500 ml As(V) solution of known concentration and the adsorbent (bone char), which was weighed and added to the solution. Each beaker was removed after the required reaction time and the solution was filtered through qualitative filter paper, and the supernatant was analyzed for its arsenic ions. Each experiment was run in triplicate and mean values were reported. All experiments were carried out at room temperature ($28 \pm 2\,°C$).

To study the effect of initial pH (2–13) on arsenic uptake by bone char, experiments were performed with initial arsenic concentrations of 0.5, 1.0 and $1.5\,mg\,l^{-1}$ and adsorbent dose of $0.6\,g\,l^{-1}$ at a fixed contact time of 30 min. The effect of contact time was studied with an initial arsenic concentration of 0.5, 1.0 and $1.5\,mg\,l^{-1}$ and bone char of $0.6\,g\,l^{-1}$; pH was kept at 10 and contact time was varied from 10 to 60 min. The effect of dosage of bone char was studied by varying the dose from 0.1 to $0.8\,g\,l^{-1}$ at a fixed pH of 10 with an

initial As(V) concentration of 0.5, 1.0 and $1.5\,mg\,l^{-1}$ and a contact time of 30 min.

3. Results and discussion

3.1. Effect of pH

In order to determine the desired pH for adsorption of As(V) over bone char, the uptake of As(V) as a function of hydrogen ion concentration was studied. The duration of arsenic adsorption was kept 30 min. Fig. 1 showed that the optimum adsorption was achieved in the pH range between 9 and 13 for initial As(V) concentration of 0.5, 1.0 and $1.5\,mg\,l^{-1}$. High adsorption percentage was observed at higher pH values. After adsorption the pH of solution was slightly climb up.

One reason for the change of pH may be ion exchange. And the reason for the higher adsorption efficiency at higher pH maybe the formation of hydroxyl groups and the co-precipitation between calcium hydrogen arsenate and hydroxylapatite in the aqueous solution on the surface of the bone char. And the pH of the solution determined the concentration distribution of the ionic forms of the As(V).

3.2. Effect of adsorbent dose

The effect of adsorbent dose on As(V) uptake was depicted in Fig. 2, which showed that adsorption efficiency of As(V) increased very rapidly with an increase in dosage of bone char from 0.1 to $0.6\,g\,l^{-1}$; a marginal increased was observed on further increase in the adsorbent dose. At $0.8\,mg\,l^{-1}$ bone char, maximum removal efficiencies of 98.54% were observed at temperature of 28 °C (301 K). The increase in the efficiency of removal may be attributed to the fact that with an increase in the adsorbent dose, more adsorbent surface, or more adsorption spots were available for the solute to be adsorbed. And with the increase of temperature from 28 °C (301 K) to 48 °C (321 K), the adsorption efficiency of As(V) decreased a little.

3.3. Adsorption kinetics study

The contact time dependence figure of arsenic adsorption for three concentrations by bone char was illustrated in Fig. 3. For each of these initial concentrations, a relatively rapid adsorption took place during the first 30 min, followed by a slow sorption which lasted 20–30 min. At initial arsenic concentration of 0.5, 1.0, and $1.5\,mg\,l^{-1}$, 95.2, 86.74, and 83.8% As(V) removal were obtained, respectively in the first 30 min at pH 10, and the removal percentage
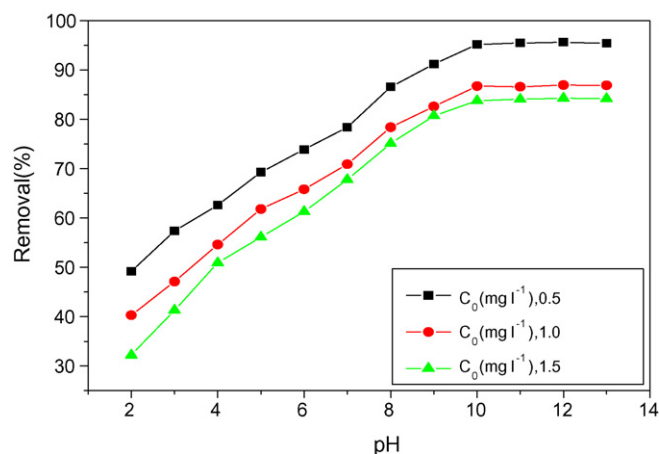
Table 1
Physical and chemical properties of bone char

Physical properties		Chemical composites	
Items	Limits	Items	Limits
Bulk density (dry)	$655\,kg\,m^{-3}$	Acid insoluble ash	3 wt% max
Carbon surface area	$52\,m^2\,g^{-1}$	Calcium carbonate	7–9 wt%
Total surface area	$150\,m^2\,g^{-1}$	Calcium sulfate	0.1–0.2 wt%
Pore volume, V_p	$0.23\,cm^3\,g^{-1}$	Carbon content	9–11 wt%
Moisture	5 wt% max	CaHAP	70–76 wt%

Fig. 1. The pH dependence for As(V) adsorption on bone char. Adsorbent dose: $0.6\,g\,l^{-1}$; initial As(V) concentrations: 0.5, 1.0, $1.5\,mg\,l^{-1}$; contact time: 30 min.

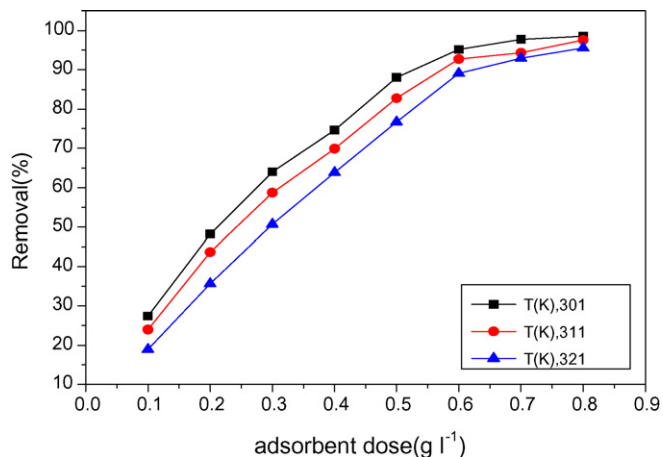**Fig. 2.** The dosage of adsorbent dependence for As(V) adsorption on bone char. Initial As(V) concentrations: 0.5 mg l^{-1}; contact time: 30 min; pH 10.

reached 99.18% at adsorption equilibrium time at the initial As(V) concentration of 0.5 mg l^{-1}.

The results obtained from the experiments were used to study the rate-determining step in the adsorption process. The adsorption rate constant (k_{ad}) for adsorption was determined from the following first-order rate expression [23]:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_{ad}}{2.303}\right)t \tag{1}$$

where q_e and q_t (both in mg g^{-1}) were the amount of As(V) adsorbed per unit mass of bone char at equilibrium and time t, respectively, and k_{ad} is the rate constant (min^{-1}). The value for k_{ad} was calculated from the slope of the linear plot of $\log(q_e - q_t)$ vs. t (Fig. 4). The adsorption rate constant was 0.14 min^{-1} and was independent of initial As(V) concentration.

In case of strict surface adsorption, a variation in rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of adsorption will not be linear [24]. Besides for adsorption on the outer surface of adsorbent, there is also a possibility of transport of adsorptive ions from the solution to the pores of the adsorbent due to stirring on batch process. This possibility was tested in terms of a graphical relationship between amount of As(V) adsorbed and square root of time t (Fig. 5). In order to show the existence of intraparticle diffusion in the adsorption process, the amount of As(V) sorbed per unit
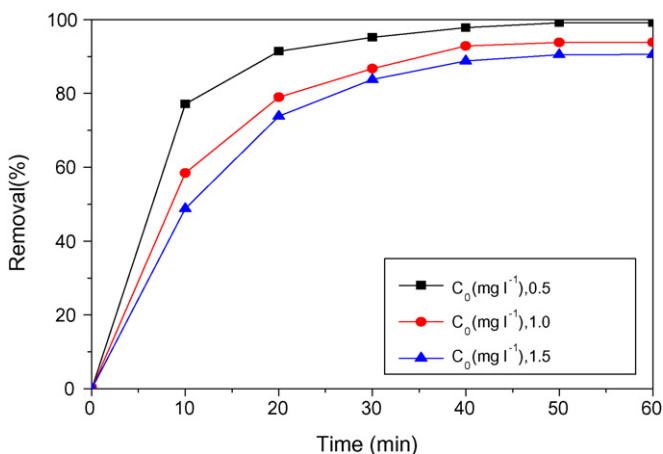

Fig. 3. The contact time dependence for As(V) adsorption on bone char. Adsorbent dose: 0.6 g l^{-1}; initial As(V) concentrations: 0.5, 1.0, 1.5 mg l^{-1}; pH 10.
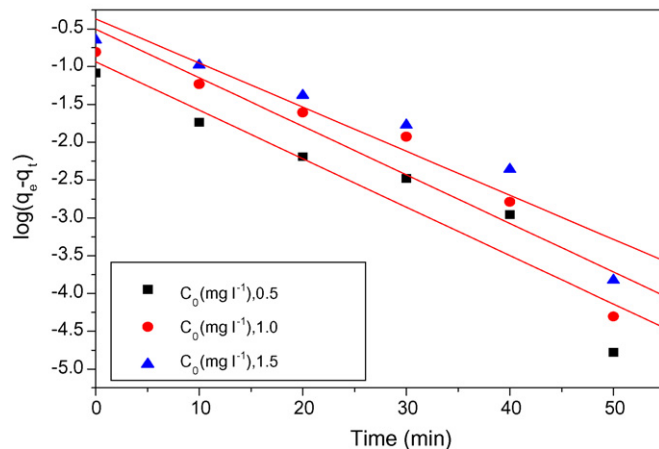

Fig. 4. Lagergren plot for As(V) adsorption of on bone char. Adsorbent dose: 0.6 g l^{-1}; initial As(V) concentrations: 0.5, 1.0, 1.5 mg l^{-1}; corresponding correction coefficient of the three linear plot: 0.94, 0.95, 0.95; pH 10.

mass of adsorbents at time t, q_t was plotted as a function of square root of time, $t^{0.5}$.

The rate constant for the intraparticle diffusion was obtained using the equation:

$$q_t = K_p t^{0.5} \tag{2}$$

where K_p (mg g^{-1} min$^{-0.5}$) is the intraparticle diffusion rate constant. The plot for intraparticle diffusion showed that initially curved portion reflected film or boundary layer diffusion effect and the subsequent linear portion attributed to the intraparticle diffusion effect [25]. K_p values were obtained from the slope of the linear portion of the curve at each solute concentration. The K_p values were found to be as 0.004, 0.013, and 0.022 mg g^{-1} min$^{-0.5}$ at initial As(V) concentration of 0.5, 1.0, and 1.5 mg l^{-1}, respectively, which depicted that intraparticle diffusion was slow and rate-determining step. This suggests that the adsorption was governed by the diffusion within pores of the adsorbent. The linear portions of the curves did not pass through the origin (Fig. 5). This indicated that mechanism of arsenate removal on bone char was complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate-determining step [26].

3.4. Adsorption mechanisms

The Fourier transform infrared spectroscopy (FTIR) has been considered as a kind of direct means for investigating mechanisms
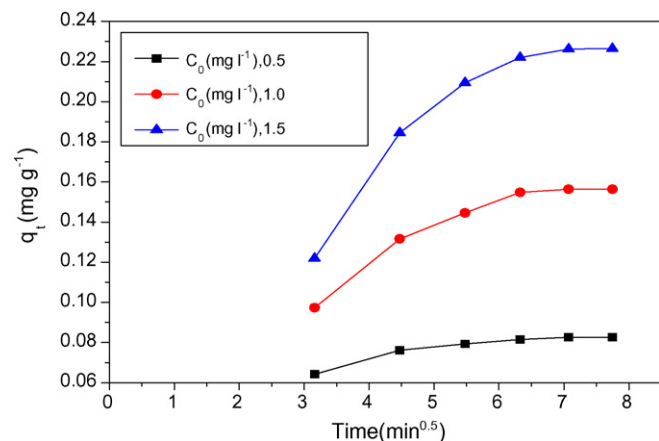

Fig. 5. Intraparticle mass transfer curve for As(V) adsorption of on bone char. Adsorbent dose: 0.6 g l^{-1}; initial As(V) concentrations: 0.5, 1.0, 1.5 mg l^{-1}; pH 10.
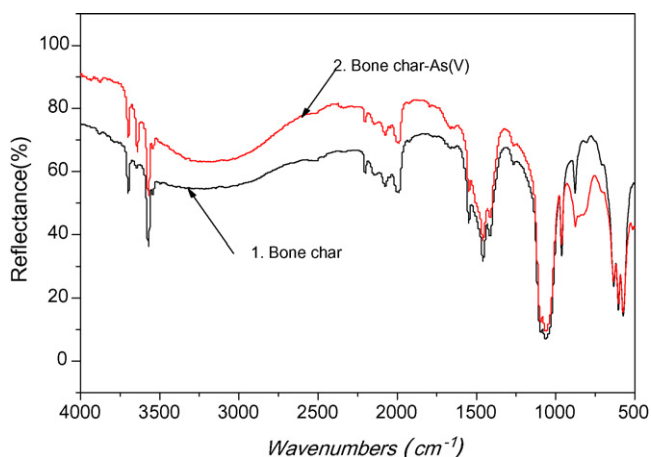
Fig. 6. FTIR spectra of (1) bone char; (2) bone char after As(V) adsorption.
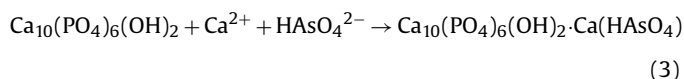
of arsenic adsorption [27]. FTIR of bone char before and after As(V) binding adsorption at pH 10 were shown in Fig. 6. The absorption around 3570 cm^{-1}, found in both the two spectra was OH associated by hydrogen bond stretch, which is the typical band for hydroxylapatite [28,29].

At another hand, a divalent anion HAsO$_4^{2-}$ dominates at pH values of 8–11 [30]. Ca–OH attaching at bone char is a cation, which would combine with HAsO$_4^{2-}$ anion. A strong band at wave number of 876 cm^{-1}, which corresponded to the bending vibration of HAsO$_4^{2-}$, was observed from the spectra after adsorption (Fig. 6). Here, as a frame or seed crystal, bone char immobilizes Ca–OH, and furthermore HAsO$_4^{2-}$. And it occurred the co-precipitation between calcium hydrogen arsenate and hydroxylapatite in the aqueous solution was part of responsibility for the precipitation of As(V) on the surface of the adsorbent, so to remove arsenic from aqueous solution.
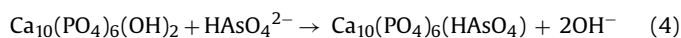
The narrow appearance from 3650 to 3584 cm^{-1} in both spectra is the dissociative O–H [29]. After the adsorption of arsenic to bone char, the band at 3650 cm^{-1} was shifted to 3640 cm^{-1} and the band intensity also increased due to the replacement of OH anions of the Ca–OH with anions during the exchange reaction. That was offered to account for why after the adsorption of As(V) to bone char, the pH of solution was a litter high than before. In aqueous environment at pH value of 9–13, calcium hydroxide can generate water-soluble functional groups such as Ca–OH. It is interesting to know that not only solid-state functional group, but also water-soluble functional group is effective for the apatite nucleation [31], which attaches at bone char.

In a word, the removal of As(V) was adsorption co-precipitation and ions exchange:

Adsorption:

$$Ca_{10}(PO_4)_6(OH)_2 + Ca^{2+} + HAsO_4^{2-} \rightarrow Ca_{10}(PO_4)_6(OH)_2 \cdot Ca(HAsO_4) \tag{3}$$

Ion exchange:

$$Ca_{10}(PO_4)_6(OH)_2 + HAsO_4^{2-} \rightarrow Ca_{10}(PO_4)_6(HAsO_4) + 2OH^- \tag{4}$$

4. Conclusions

Bone char was a suitable adsorbent for the removal of As(V) from aqueous solution. The adsorption was found to be strongly dependent on pH, dosage of adsorbent, and contact time. A maximum of 99.18% As(V) removal could be achieved at the initial As(V) concentration of 0.5 mg l^{-1} at pH 10. The adsorption pro-

cess followed a first-order kinetics equation. The results suggested that the removal of As(V) on bone char was complex mechanism where both co-precipitation between calcium hydrogen arsenate and hydroxylapatite in the aqueous solution and ions exchange between calcium hydrogen arsenate and hydroxyl ion. And the adsorption process followed a first-order kinetics equation.

In order to realize its full potential as a commercial sorbent, uptake of arsenic under continuous condition with industrial wastewater containing such toxic metals must be evaluated. Currently such an investigation is being undertaken.

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