

Adsorption isotherm and kinetic studies of As(V) removal from aqueous solution using cattle bone char

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ABSTRACT

The As(V) adsorption onto bone char was investigated as a function of bone char dosage, pH and contact time in batch tests. The initial As(V) concentrations were varied from 0.1 to 1 mg/L to evaluate the adsorption kinetics and isotherm. The As(V) concentrations were analyzed using a graphite furnace atomic absorption spectrophotometer. The highest As(V) removal was found to be 62% after 3 d using 3 g bone char at a pH level of 4.0 for 0.5 mg/L As(V) concentration. The maximum adsorption capacity was 0.13 for 1 mg/L As(V) concentration. A Langmuir isotherm and second order adsorption kinetics were observed for As(V) adsorption.

Key words | adsorption, arsenic, bone char, isotherm, kinetics

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ABBREVIATIONS

ANOVA	Analysis of variance
CaHA	Calcium hydroxyapatite
GF-AAS	Graphite furnace atomic absorption spectrophotometer
HSD	Honestly significant difference
PES	Polyethersulfone
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

INTRODUCTION

Arsenic pollution in natural water is a worldwide problem. In recent years, major arsenic contamination has been found in the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan, Afghanistan, Cambodia, Pakistan, Nepal, and India (Mukherjee *et al.* 2006). The World Health Organization (WHO) has limited the arsenic concentration in drinking water to be 0.01 mg/L (WHO 2011). It was demonstrated that more than 140 million people in the world

consume groundwater with arsenic concentration above the WHO standard (Liu *et al.* 2010). About 13 million people in the United States are exposed to drinking water with arsenic levels greater than 0.01 mg/L (Bissen & Frimmel 2003). According to the United States Environmental Protection Agency, inorganic arsenic is considered as the number one toxin of the prioritized pollutants (Ahmad 2001; Ng *et al.* 2003). Long exposure to very low concentrations causes cancer of skin, lungs, bladder and kidney, in addition to skin pigmentation changes, skin thickening, neurological disorders, muscular weakness, loss of appetite, and nausea. Acute poisoning typically causes vomiting, esophageal/abdominal pain, and bloody 'rice water' diarrhea (Mohan & Pittman 2007). Arsenic is present in water primarily as trivalent arsenite – As(III) and pentavalent arsenate – As(V) although As(V) is more abundant than As(III) in many groundwater systems (Mandal & Suzuki 2002). In addition, As(V) is more easily adsorbed by activated carbon than As(III) (Diamadopoulos *et al.* 1992).

Among various treatment methods, adsorption is the most widely applied physico-chemical treatment process

for removing pollutants from aqueous media (Choy & McKay 2005; Mobasherpour *et al.* 2011). The benefits of the adsorption method include its high removal efficiency, low cost, easy operation, lower environmental effects, regeneration potential of the adsorbents, and less energy and chemical requirements (Mohan & Pittman 2007; Sarkar *et al.* 2010). The most commonly used adsorptive media are activated carbon, activated alumina, and iron-oxide-based media. However, they are very expensive and not suitable for developing countries (Mobasherpour *et al.* 2011).

In recent years, the use of bone char has received much attention as an adsorbent because it is relatively cheap and has demonstrated the ability to remove many metal ions (Choy & McKay 2005; Pan *et al.* 2009; Smiciklas *et al.* 2010; Dawlet *et al.* 2013). Bone char is a product of pyrolysis of ground bone heated at high temperature with limited oxygen supply (Pan *et al.* 2009; Lurtwitayapont & Srisatit 2010). Large amounts of bones are generated from cattle, goat, sheep, and chicken as waste materials. The conversion of this bone into bone char is an environmental and waste control measure (Dawlet *et al.* 2013). The main components of the bone char are calcium hydroxyapatite (CaHA), carbon, and calcium carbonate (Pan *et al.* 2009). The adsorption properties of CaHA make it able to remove inorganic ions from aqueous solution (Tanaka *et al.* 2005). However, bone char has been rarely investigated as an adsorbent for As(V) removal from aqueous systems (Dong *et al.* 2011; Mohan *et al.* 2011). Hence, a significant knowledge gap exists for the use of this low-cost biomass derived material as a possible economically viable adsorbent to remove As(V) from aqueous systems.

Consequently, the main objective of the present research was to investigate the removal efficiency of As(V) from aqueous solution using bone char generated from the calcination of cattle bone. The secondary objective was to identify the effects of the operational parameters, including adsorbent dose, pH, and contact time for the maximum As(V) removal from the wastewater, and also to perform equilibrium, isotherm, and kinetics studies for As(V) removal. The outcome of this project will help people to obtain drinking water with an allowable level of arsenic using a low-cost technology.

MATERIALS AND METHODS

Reagents

Analytical grade chemicals and deionized (DI) water were used to prepare all testing solutions. The As(V) stock solution of 1,000 mg/L was prepared by dissolving 4.16 g of sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) (Sigma Aldrich, MO, USA) in 1,000 mL of DI water. The stock solution was subsequently diluted to obtain various arsenic concentrations as required. The diluted solutions were then used during the batch tests to determine the effects of different parameters on the removal of As(V) and also to evaluate the kinetics and isotherm of the As(V) adsorption process from aqueous solutions.

Adsorbent

Bone char purchased from Anthracite Filter Media Co. (AFM), Culver City, California, USA was used as an adsorbent. Bone char was prepared through calcining cattle bones at a temperature of 450 °C. Chemical properties of the bone char supplied by the company are hydroxyapatite of 70–76%, carbon content of 9–11%, calcium carbonate of 7–9% and calcium sulfate of 0.1–0.2%. In addition, total surface area, pore volume, and particle size of the bone char are 100 m²/g, 0.225 cm³/g, and 250–480 μm, respectively. Bone char was used in batch tests without any pretreatment.

Effects of adsorbent dosage on As(V) removal

To identify the effect of adsorbent dosage, batch sorption experiments were conducted in Erlenmeyer flasks with 200 of 0.5 mg/L synthetic As(V) solution. The pH of the solution was adjusted to 7 by adding either 1 M NaOH or 0.5 N H₂SO₄. About 1, 2, 3, 4, and 5 g/L of bone char were added in different flasks. The flasks were then placed in a digital platform shaker (Innova 2300/2350) at 150 rpm for 7 d at room temperature. About 2 mL samples were collected periodically using separate syringes during batch tests. Collected samples were filtered immediately through a 0.2 μm polyethersulfone (PES) syringe filter (Sterlitech Co., WA, USA) to get rid of any bone char particles from samples. Filtered samples were

then analyzed for residual As(V) concentration using a graphite furnace atomic absorption spectrophotometer (GF-AAS) (Model: 210VGP, 220GF, Buck Scientific, Inc.) with an arsenic hollow cathode lamp at a slit of 7 nm and wavelength of 193.7 nm. The GF-AAS was calibrated regularly prior to the sample analysis. Known samples were run throughout testing to ensure accuracy and quality control. Unknown samples were measured five times and the average value of As(V) concentrations is presented in this paper. Samples were analyzed on the same day or preserved at 4 °C and pH lower than 2 if needed. The percentage removal of As(V) was determined using the following equation:

$$\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100$$

Effects of pH on As(V) removal

Batch sorption experiments were conducted in a similar manner to that described above with the exception of maintaining pH from 1 to 11 in different flasks. The optimum amount of bone char obtained from the above tests was added in all flasks.

Effects of initial As(V) concentration on adsorption capacity

Further batch tests were conducted in a similar manner to that described in the above sections with the exception of

the variation of initial As(V) concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 mg/L. During tests, the amount of bone char and initial pH value were maintained at the optimum level.

Statistical analysis

The effects of bone char dosage and pH on the adsorption of As(V) onto the bone char were statistically analyzed using the one-way analysis of variance (ANOVA) test at a 95% confidence level. If the ANOVA test provided a *P*-value less than 0.05, further analysis was performed using a Tukey honestly significant difference (HSD) test for multiple comparisons of the means to identify significantly different values.

RESULTS AND DISCUSSION

Effects of adsorbent dosage on As(V) removal

Batch tests were conducted at pH 7 with the variation of bone char dosages from 1 to 5 g/L for 7 d. The percentage of As(V) removal for different bone char dosages with time is shown in Figure 1(a). The As(V) removal improved with an increase of bone char dosages from 1 to 3 g/L. However, there was no significant increase in As(V) removal above bone char dosages of 3 g/L which indicates that the adsorption capacity of the bone char does not only depend on the surface area of the adsorbent but also other parameters (Hadi et al. 2015; Salam 2015) which need further

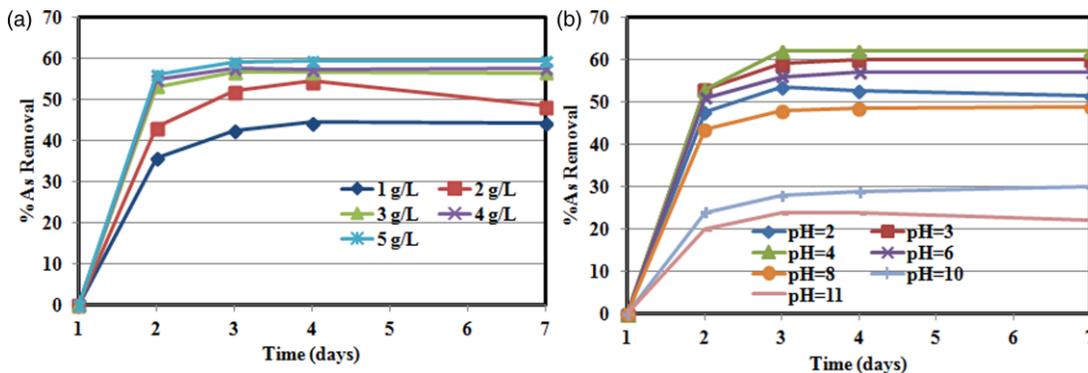


Figure 1 | As(V) removal efficiencies onto bone char as adsorbent with (a) different dosages of bone char at pH of 7, initial As(V) concentration of 0.5 mg/L, and (b) different pHs at initial As(V) concentration of 0.5 mg/L, bone char of 3 g.

investigation. The As(V) removal improved until 3 d for all bone char dosages. Then a relatively stable value was obtained until the end of the test. The percentages of As(V) removal were 43%, 52%, 56%, 57% and 58% for bone char dosages of 1 g/L, 2 g/L, 3 g/L, 4 g/L and 5 g/L, respectively, in 3 d (Figure 1(a)). The statistical analysis using the Tukey HSD test indicated that there were no significant differences in percentage of As(V) removal between 3 and 4 g/L ($1.0379 < \text{HSD} = 6.73$), 3 and 5 g/L ($2.7034 < \text{HSD} = 6.73$) of bone char dosages. However, the percentage of As(V) removal was significantly different in all other cases. Therefore, the bone char dosage of 3 g/L was used for further studies.

Effects of pH and reaction time on As(V) removal

pH is an important parameter in the adsorption process. pH has effects on the surface charge of adsorbent, chemical species, and the degree of ionization of surface functional groups (Li et al. 2014). To identify the effect of pH value, further tests were performed using bone char dosage of 3 g/L with the variation of pH from 1 to 11 at an initial As(V) concentration of 0.5 mg/L.

The percentage of As(V) removal was increased with the increase of pH from 2 to 4 as shown in Figure 1(b). Subsequently, the percentage of As(V) removal reduced for all pH values higher than 4. The minimum As(V) removal was observed to be 20% at pH 11 whereas the As(V) removal reached the highest value of 62% at pH 4. Since the highest removal of As(V) was obtained at pH 4, further studies were conducted using a pH value of 4. Similar results were also achieved by other researchers (Saha et al. 2005; Kizilkaya et al. 2010). The statistical analysis was performed to observe the effect of pH on As(V) removal. The percentages of As(V) removal did not differ significantly for pH values between 2 and 3, 2 and 6, 2 and 8, 3 and 4, 3 and 6, and 4 and 6. However, there were significant difference in As(V) removal for all other cases.

As(V) adsorption is favored in acidic pH. Arsenic removal by most of the adsorbents increases somewhat as pH is decreased (Mohan & Pittman 2007). In acidic solution, the surface of CaHA is positively charged due to $-\text{CaOH}^{2+}$ and neutral $-\text{POH}^0$ sites on the surface (Pan et al. 2009). The predominant species of As(V) in acidic

solution is H_2AsO_4^- which is subjected to an electrostatic attraction with the positively charged surface resulting in an adsorption (Zhu et al. 2009). On the other hand, increasing pH causes the surface of CaHA to become negatively charged because of OH^- consumption via deprotonation of surface $\equiv\text{CaOH}^{2+}$ and $\equiv\text{POH}^0$ sites leading to a neutral $\equiv\text{CaOH}^0$ and negatively charged RPO^- species on the surface (Pan et al. 2009). At alkaline pH, As(V) species are HAsO_4^- and AsO_4^{3-} (Lorenzen et al. 1995) which show electrostatic repulsion with the negatively charged surface and thus decrease the adsorption at high pH (Zhu et al. 2009).

For all pH values, the percentage of As(V) removal was increased with the increase of time until 3 d. Then, the As(V) removal reached a relatively stable value until 7 d (Figure 1(b)). Similar results were also observed for all bone char dosages illustrated earlier. Therefore, the optimum reaction time is considered to be 3 d. Zhu et al. (2009) also observed similar results.

Effects of initial As(V) concentration on adsorption capacity

The As(V) concentrations in mg/L at equilibrium (C_e) and at any particular time (C_t) were evaluated for different initial As(V) concentrations (C_0) of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 mg/L. The pH and bone char dosage were maintained constant at the optimum value. The adsorption capacities of bone char at any particular time (q_t) and at equilibrium (q_e) were calculated using concentrations of C_0 , C_e , and C_t according to the mass balance Equations (1) and (2) shown below, respectively (Mohan & Pittman 2006). Afterward, these adsorption capacities (q_e , q_t) were used to determine the equilibrium adsorption isotherms and the kinetics model plots.

$$q_t = \left(\frac{C_0 - C_t}{m} \right) V \quad (1)$$

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V \quad (2)$$

where V is the volume of the solution in litres (L), and m is the dry mass of bone char in grams (g).

Figure 2 represents the adsorption capacity of As(V) onto the bone char at initial As(V) concentrations ranging

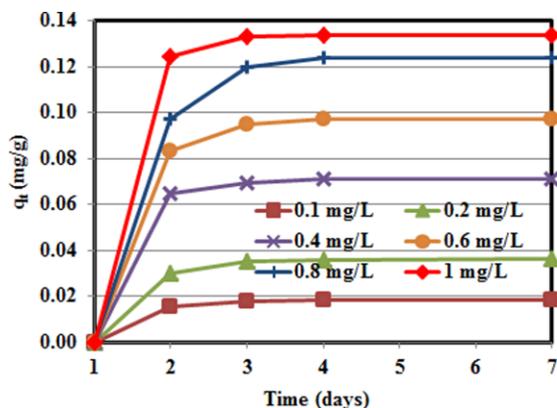


Figure 2 | Adsorption capacities of bone char with time for different initial As(V) concentrations. pH: 4; bone char: 3 g.

from 0.1 to 1 mg/L. The adsorption capacity of As(V) is highly dependent on the initial As(V) concentration. The As(V) was adsorbed on the bone char in the first 2 d at a faster rate. A slight uptake of As(V) was observed up to an equilibrium level in 3 d for all initial As(V) concentrations. The As(V) adsorption capacity at equilibrium increased from 0.018 to 0.134 mg/g with the increase of the initial As(V) concentration from 0.1 to 1 mg/L.

At higher initial As(V) concentrations, adsorbent and As(V) may collide frequently and generate a higher driving force to overcome all mass transfer resistances between the aqueous and solid phases (Aksu & Tezer 2005) resulting in a higher adsorption capacity. The maximum adsorption capacities of As(V) onto various bio-based adsorbents are illustrated in Table 1. The variation of adsorption capacities

Table 1 | Summary of As(V) adsorption capacity of various bio-based adsorbents

Adsorbent type	q_m (mg/g)	References
Cattle bone char	0.134	This study
Rice husk biochar (RHB)	7.1	Samsuri <i>et al.</i> (2013)
Fe(III) coated RHB	16.9	Samsuri <i>et al.</i> (2013)
Iron oxide amended rice husk char	0.606 ± 0.065	Cope <i>et al.</i> (2014)
Leonardite char	8.4	Chammui <i>et al.</i> (2014)
Coal based activated carbon	1.76	Li <i>et al.</i> (2014)
Biochar/ γ -Fe ₂ O ₃ composite	3.147	Zhang <i>et al.</i> (2013)
Sponge iron char	0.0289	Yadav <i>et al.</i> (2014)

among bio-based adsorbents might be due to different surface properties of the adsorbents.

Evaluation of adsorption isotherm

The adsorption isotherms of As(V) onto bone char were evaluated using Langmuir and Freundlich models which are expressed linearly in Equations (3) and (4), respectively (Freundlich 1906; Langmuir 1916).

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

$$\text{Log}(q_e) = \frac{1}{n} \text{Log}(C_e) + \text{Log}(K_F) \quad (4)$$

where C_e denotes the equilibrium As(V) concentration in mg/L, q_e represents the equilibrium adsorption capacity of bone char in mg/g, q_m is the maximum adsorbed amount of As(V) per mass of bone char in mg/g, K_L is the Langmuir equilibrium adsorption constant (L/mg) related to the free energy of adsorption, K_F is the Freundlich constant [(mg/g)(L/mg)^{1/n}] related to the strength of the adsorptive bond (Gupta *et al.* 1998), and $1/n$ is the adsorption intensity factor or surface heterogeneity (unit-less).

The Langmuir isotherm indicates the free energy of adsorption which is independent of the surface coverage of adsorption sites. The surface saturation of solids occurs due to a monolayer coverage of adsorbate (Khezami & Capart 2005). The values of $1/q_e$ were plotted against $1/C_e$ to evaluate the Langmuir isotherm. The values of K_L and q_m were calculated using the slope and intercept of the best fit line, respectively. In addition, the values of $\log q_e$ and $\log C_e$ were plotted to assess the Freundlich isotherm parameters of $1/n$ and K_F . The Freundlich constant, K_F , represents the quantity of adsorbed metal ions for a unit equilibrium concentration (i.e. $C_e = 1$) (Benjamin 1978). The Langmuir and Freundlich isotherms were evaluated based on the regression coefficients (R^2) values. The isotherm that had an R^2 value closest to 1.0 was selected as the operating sorption isotherm and used for modeling of the sorption of As(V) onto the bone char. The important characteristics of Langmuir sorption can be presented using a dimensionless separation factor, R_L , which is

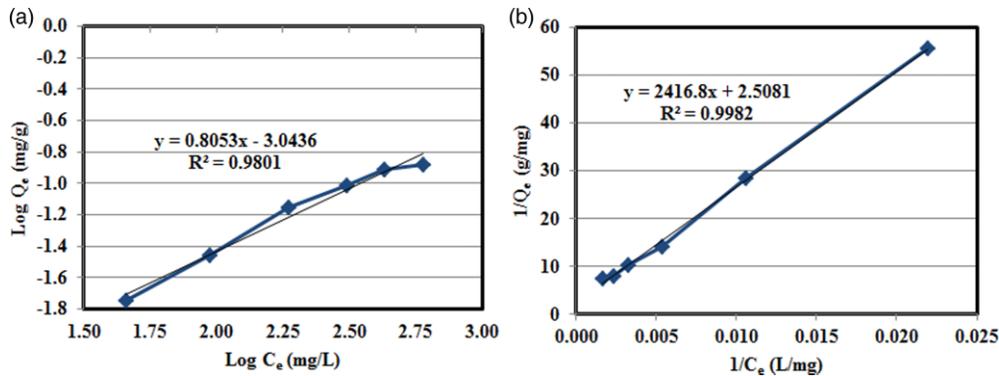


Figure 3 | Plots of (a) Freundlich and (b) Langmuir isotherms for As(V) sorption onto bone char. pH: 4; bone char: 3 g.

expressed in Equation (5) (Arulkumar *et al.* 2012)

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (5)$$

where K_L (L/mg) and C_0 (mg/L) are the Langmuir constant and initial adsorbate concentration, respectively. The adsorption process is irreversible if $R_L = 0$, favorable if $R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$ (Khezami & Capart 2005).

Figure 3(a) and 3(b) represent the Freundlich and Langmuir models, respectively, for the adsorption isotherm of As(V) from liquid onto bone char. The adsorption data over an As(V) concentration range from 0.1 to 1 mg/L were better represented by the Langmuir model ($R^2 = 0.9982$) than the Freundlich model ($R^2 = 0.9801$).

The value of R_L ($0.998 < 1$), the essential characteristic of Langmuir dimensionless separation factor or equilibrium parameter, indicates the favorable adsorption process of As(V) onto the bone char (Hameed *et al.* 2009). The suitability of the Langmuir model indicates monolayer coverage of the As(V) onto the homogenous surface of bone char with a finite number of identical sites. As(V) species did not interact with each other during the adsorption process (Dong *et al.* 2011). Similar results were also observed for Cr(III), Pb(II), and Cr(VI) adsorption onto the bone char by other researchers (Wilson *et al.* 2001; Lurtwitayapont & Srisatit 2010; Hyder *et al.* 2014). However, Pan *et al.* (2009) and Dawlet *et al.* (2013) explained the adsorption of Hg(II) and Co(II) onto the bone char using the Freundlich model. The variation of the results might be due to the difference in interactions between adsorbates

and bone chars (Samsuri *et al.* 2013). The value of n obtained from the Freundlich isotherm was greater than 1 (Table 2), indicating that As(V) has a good adsorption potential to the bone char (Kadirvelu & Namasivayam 2000; Lurtwitayapont & Srisatit 2010). The adsorption isotherm constants determined from both isotherm models are listed in Table 2.

Evaluation of adsorption kinetics

The adsorption reaction kinetics of As(V) onto the bone char were analyzed with the pseudo first-order kinetic (Equation (6)) and second-order kinetic (Equation (7)) models (Lagergren 1898; Ho & McKay 1999).

$$\log(q_e - q_t) = -\frac{K_1}{2.303}t + \log q_e \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2} \quad (7)$$

where q_e and q_t represent the adsorption capacities (mg/g) of bone char at equilibrium and at a particular time t (h), respectively. The rate constants for the pseudo first-order and second-order kinetics are denoted by K_1 (h^{-1}) and K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$), respectively.

The linear plot of $\log(q_e - q_t)$ vs time (t) gives values of K_1 and q_e for the pseudo first-order kinetic model whereas

Table 2 | Adsorption isotherm constants of As(V) onto bone char

Freundlich isotherm	Langmuir isotherm
$R^2 = 0.9801$	$R^2 = 0.9982$
$1/n = 0.8053$	$q_m = 0.399$ (mg/g)
$K_F = 0.0009$ (mg/g). (L/mg) ^{1/n}	$K_L = 0.00104$ (L/mg)

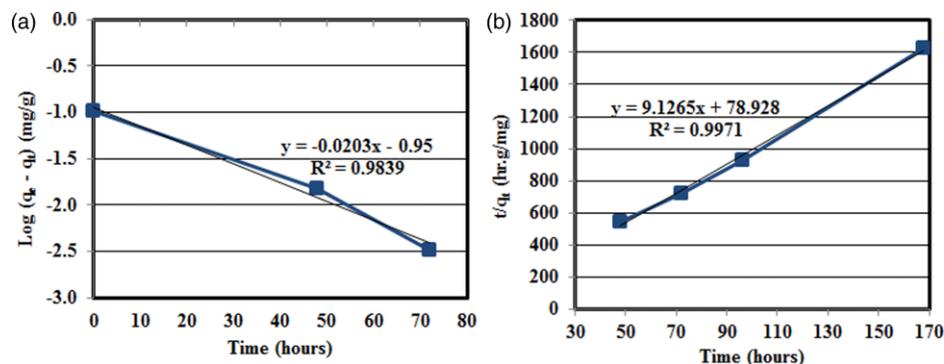


Figure 4 | Plots of (a) first-order and (b) second-order kinetic models for As(V) sorption onto bone char. pH: 4; bone char: 3 g; initial As(V) concentration: 0.5 mg/L.

the plot of t/q_t against time (t) provides values of K_2 and q_e for the pseudo second-order kinetic model. The regression coefficients (R^2) of the first- and second-order kinetic models were compared to identify which model is suitable for As(V) adsorption onto the bone char.

Figure 4(a) and 4(b) represent the kinetic adsorption data for As(V) removal using the bone char based on the pseudo first-order and pseudo second-order kinetic models, respectively. The adsorption process of As(V) onto the bone char revealed a best fit to the pseudo second-order kinetic model ($R^2 = 0.9839$) compared to the pseudo first-order kinetic model ($R^2 = 0.9971$) for an initial As(V) concentration of 0.5 mg/L.

Since the experimental data follow the pseudo second-order kinetic model, the uptake of As(V) onto the bone char could take place due to chemisorption. It can occur through the sharing of valency forces or the exchange of electrons between the adsorbate and the bone char. As a result, new chemical species of As(V) can form on the surface of the bone char and finally be removed from the liquid phase (Dong *et al.* 2011; Mohan *et al.* 2011). Moreover, the pseudo second-order kinetic model indicates that the adsorption reaction of As(V) on the bone char depends on the concentration of As(V) in solution and the amount of

bone char needed to adsorb the As(V) ions from solution at equilibrium. Kinetic parameters and correlation coefficients of the two models tested are summarized in Table 3. The pseudo second-order model was also followed for the adsorption kinetic of Co(II) and Cr(VI) onto bone char (Pan *et al.* 2009; Hyder *et al.* 2014).

CONCLUSIONS

In this research, adsorption of As(V) ions from aqueous solution was investigated using cattle bone char. The maximum percentage of As(V) removal occurred at bone char dosage of 3 g/L, contact time of 3 d and pH of 4. The adsorption capacity of the bone char reached the highest value of 0.13 mg/g for an initial As(V) concentration of 1 mg/L after 3 d. The adsorption isotherm of As(V) closely fit the Langmuir model with a regression coefficient (R^2) of 0.9982. The kinetics of As(V) adsorption followed the pseudo-second order reaction with R^2 values greater than 0.99. The results obtained in this study suggest that bone char has the potential to be an economical adsorbent for As(V) removal from water and wastewater resources.

Table 3 | Coefficients of the kinetic models of As(V) adsorption onto bone char

First-order kinetic model	Second-order kinetic model
$R^2 = 0.9839$	$R^2 = 0.9971$
$K_1 = 0.0468 \text{ (h}^{-1}\text{)}$	$K_2 = 1.055 \text{ (g.mg}^{-1}\text{.h}^{-1}\text{)}$
$q_e = 0.1122 \text{ (mg/g)}$	$q_e = 0.1096 \text{ (mg/g)}$

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