brought to you by

DESALINATION

Desalination 249 (2009) 609-614

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Sorption of cobalt to bone char: Kinetics, competitive sorption and mechanism

Xiangliang Pan^{a,b,d}, Jianlong Wang^{c,e,1}, Daoyong Zhang^{b,d,*,2}

^a Xinjiang Institute of Ecology and Geography, Chinese Academy of Sciences, Urumuqi 830011, China

^b State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China

^c Institute of Nuclear Energy Technology, Tsinghua University, Beijing, China

^d 46 Guanshui Road, Guiyang, Guizhou, China, 550002

^e Room 401, Energy Science Building, Tsinghua University, Beijing, China, 100083

ARTICLE INFO

Article history: Accepted 30 January 2009 Available online 12 October 2009

Keywords: Bone char Adsorption Cobalt Kinetics Mechanism

ABSTRACT

Swine bone char is the combustion residues of swine bone. Cobalt adsorption to swine bone char was studied. Batch kinetics studies showed that a rapid uptake occurred during the first 5 min and was followed with a very slow intraparticle diffusion process. The sorption kinetics was ideally conformed to pseudo-second equation, indicating several mechanisms involved in the adsorption process. Equilibrium sorption isotherm studies showed that the Freundlich isotherm model satisfactorily described the sorption data. The presence of co-ions had appreciable inhibiting effects on cobalt uptake by bone char because copper and zinc had higher affinity for the bone char surface than cobalt. Calcium concentration in solution and XRD analysis showed that ion exchange was involved in the removal of Co from solution over a certain initial cobalt concentration range.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Contamination of aquatic environment by heavy metals is a worldwide environmental problem. A variety of methods are used to remove these toxic substances from effluents and industrial wastewater before discharging into a natural water body. The main treatment technologies include precipitation and coagulation, ion exchange, membrane processes and electrolytic technologies. However conventional treatment technologies like precipitation and coagulation become less effective and more expensive when situations involving high volumes and low metal concentrations are encountered [1]. The application of membrane processes and activated carbon are also restricted due to high costs. As a result, an inexpensive yet efficient adsorbent of heavy metals is desired in effluent cleanup. Recently, bone char has aroused much attention from wastewater treatment industry due to its advantages over other adsorbents. One advantage is that bone char is relatively inexpensive since it is made from spent bone. The other advantage is that bone char has been demonstrated as a versatile adsorbent for a wide variety of pollutants, including heavy metals, fluoride, arsenate and dyes [2–8]. Bone char is a product of pyrolysis of ground bone at over 800 °C in a limited supply of oxygen (O_2) . It is

¹ Tel./fax: +861062784843.

mainly composed of calcium hydroxyapatite (CaHA), carbon and calcium carbonate. The hydroxyapatite has a good ability to remove inorganic cations [9], which has led to the development of its use in removing heavy metals from contaminated water [2].

Cobalt is widely present in various industrious wastewater including petrochemical wastewater, cobalt-bearing mineral mining and smelting wastewater and nuclear wastewater. Acute exposure to cobalt can induce nausea, vomiting and neurotoxicological symptoms such as headaches and changes in reflexes [10]. Chronic exposure to cobalt can induce partial or complete loss of smell, gastrointestinal troubles and dilation of the heart [10]. The objectives of this study were to examine the ability of bone char to remove cobalt (II) from an aqueous solution and the mechanisms of adsorption were also investigated.

2. Materials and methods

2.1. Preparation of bone char

Swine bone was boiled for 10 min and the meat attached on the bone was removed. The bone char was produced as the modified method described by Lambert and Graham [11]. The bone was crushed into small fragments and burned by calcination in an electric muffle furnace programmed to reach 800 °C at 2 °C min⁻¹, and further calcined at 800 °C for 4 h. The residues were washed with generous deionized water in order to remove soluble inorganic ions. After it was dried at 60 °C for 24 h, bone char was powdered and sieved through a 80 mesh sieve(<180 μ m).



^{*} Corresponding author. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, PR China. Tel.: +868515890459; fax: +868515891609.

E-mail addresses: xiangliangpan@163.com (X. Pan), wangjl@tsinghua.ed.cn (J. Wang), zhang-daoyong@163.com (D. Zhang).

^{0011-9164/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.desal.2009.01.027

12

2.2. Preparation of solution

Cobalt solution was made from Analar cobalt(II) chloride 6-hydrate(CoCl₂.6H₂O). Stock solution (4000 mg l⁻¹) of cobalt ion was prepared using deionized water and subsequently diluted. The pH of the solutions was not adjusted. Cu (II) and Zn (II) were applied in the forms CuCl₂. H₂O and Zn(NO₃)₂·4H₂O diluted in deionized water, respectively.

2.3. Effect of adsorbent concentration

Bone char with various mass was added into 20 ml of 500 mg L⁻¹ cobalt solution. The suspension was shaken at 150 rpm at 25 °C. After shaking, the solution was immediately filtered through 0.22 µm filter paper. Calcium and cobalt concentrations in filtrate were measured by flame atomic absorption spectroscopy (Varian 6 AAS).

2.4. Effect of initial solution pH

The effect of pH on cobalt sorption to bone char was evaluated by adding 0.2 g of adsorbent into flasks containing 50 ml of 25 mg L⁻¹ cobalt-bearing solutions at different initial pH (2–9). pH of the solutions was adjusted using 0.1 M HCl/NaOH. Flasks were shaken at 150 rpm at 25 °C for 120 min. Initial and equilibrium pH of solutions and residual cobalt concentrations were measured.

2.5. Effect of competitive cations

The effect of competitive cations on cobalt sorption to bone char was investigated. The initial solution cobalt concentration was constant (200 mg L^{-1}) for all experiments. Concentrations of 50, 100, 150 and 250 mg L⁻¹ of Cu (II) or Zn (II) were tested for competitive uptake with cobalt by bone char. A 200 mg sample of bone char was shaken with 20 mL of binary metal solution at 150 rpm and 25 °C for 120 min. After shaking, the solution was immediately filtered through 0.22 µm filter paper. Cobalt concentrations in filtrate were measured by flame atomic absorption spectroscopy (Varian 6 AAS).

2.6. Sorption kinetics studies

The kinetic sorption experiment was carried out as follows: 2 g of bone char were added to flasks containing 100 mL of 500 mg L⁻¹ cobalt-bearing solution. Flasks were shaken at 150 rpm at 25 °C. Aliquot amounts (2 mL) of solution were collected periodically. The samples were filtered and cobalt concentrations in filtrate were determined by flame atomic absorption spectroscopy on a Varian 6 AAS.

2.7. Isothermal sorption studies

The isothermal sorption experiment was carried out as follows: A 200 mg sample of bone char was shaken with 20 mL of metal solution of varying concentration (100–1000 mg L⁻¹ Co) at 150 rpm at 25 °C for 120 min. After shaking, the solution was immediately filtered through 0.22 µm filter paper. Calcium and Cobalt concentrations in filtrate were measured by flame atomic absorption spectroscopy (Varian 6 AAS).

All the sorption tests were triplicated and the standard error values ranged from 1.5% to 4%. The mean values were used.

2.8. XRD analysis of bone char

Bone char powder before and after sorption of cobalt was analyzed by X-ray diffractometry (XRD) using a D/Max IIID diffractometer with Cu K α a radiation. Measurements were made using a step-scanning



Fig. 1. Effect of pH on cobalt sorption and final pH.

technique with the diffraction angle, 2θ , step interval of 0.05 from $5^{\circ} < 2\theta < 80^{\circ}$ and an acquisition time of 1 s per step.

3. Results and discussion

3.1. Effect of pH

Fig. 1 shows cobalt sorption capacity at different pH and the final pH of the solution. The lowest cobalt sorption capacity (6.93 mg g⁻¹) was found at an initial solution pH of 2. As the initial pH increased to 4, cobalt sorption capacity increased to 11.28 mg g⁻¹. Cobalt adsorption capacity varied little and the sorption capacity was kept constant (about 11.9 mg g⁻¹) in the initial pH range 4–8. When the initial pH was 9, the sorption capacity was increased to 12.1 mg g⁻¹, which could be attributed to the precipitation of Co(OH)₂. A study of the final pH showed that bone char exhibits excellent buffering properties. For the initial pH range 4–8, final pH values are almost kept the same value (7.2–7.6) and the sorption of cobalt is constant in this pH range. The buffering capacity of bone char could be attributed to the properties of its main component, CaHA. It was reported that acidic as well as basic solutions (in pH range 4–10) are buffered after reaction with the reactive surface sites of CaHA to its pH_{pzc} value [12,13]:

$$\equiv PO^{-} + H + \Leftrightarrow \equiv POH^{0} \tag{1}$$

$$\equiv \operatorname{CaOH}_2^+ \Leftrightarrow \equiv \operatorname{CaOH}^0 + \operatorname{H}^+ \tag{2}$$

At an initial pH below pH_{pzc} , final pH increased due to consumption of protons from the solution by the protonation of surface $\equiv PO^$ and $\equiv CaOH^0$ groups. In acidic solution, the surface charge of the CaHA was predominated by positively charged $\equiv CaOH_2^+$ and neutral $\equiv POH^0$ sites, making surface charge of HAP in this pH region positive. On the other hand, the higher initial pH (above pH_{PZC}) resulted in a decrease in final pH due to OH^- consumption via deprotonation of surface $\equiv CaOH_2^+$ and $\equiv POH^0$ sites. Consequently, neutral $\equiv CaOH^0$ and negatively charged RPO⁻ species prevailed on the surface of CaHA and CaHA surface became negatively charged [12,13].

3.2. Influence of concentration of adsorbent

As shown in Fig. 2, an increase of adsorbent concentration resulted in an increase of cobalt uptake by bone char. It was found that when the initial cobalt concentration was 500 mg L⁻¹, the cobalt removal percentage by bone char increased from 88.34% to 99.32% as bone char concentration increased from 100 mg L⁻¹ to 1000 mg L⁻¹.



Fig. 2. Influence of dosage of adsorbent on cobalt removal percentage.

3.3. Kinetics studies

Pseudo-first order equal and pseudo-second order were employed to model the sorption data over the entire time range. The pseudo-first order equation of Lagergren [14] is generally expressed as follows:

$$dq/dt = k_1(q_e - q) \tag{3}$$

where q_e and q are the amount of metal sorbed per unit weight of sorbent at equilibrium and at time t, respectively (mg g⁻¹ dry adsorbent) and k_1 the rate constant of pseudo-first order sorption (min⁻¹). Given the boundary conditions for t=0, q=0, the Eq. (3) can be integrated to give [15]

$$\log(q_{\rm e} - q) = \log q_{\rm e} - (k_1 / 2.303)t.$$
⁽⁴⁾

If the sorption process can be described by pseudo-first order equation, there should be good linear relationship between $\log(q_e - q)$ and *t*. The pseudo-second order equation assumes that the sorption process involves chemisorption mechanism and the rate of site occupation is proportional to the square of the number of unoccupied sites. If the rate of sorption is a second order mechanism, the pseudosecond order chemisorption kinetic rate equation is expressed as [15]

$$dq / dt = k_2 (q_e - q)^2 \tag{5}$$

where k_2 is pseudo-second order rate constant (g mg⁻¹ min⁻¹).

After integrating and applying boundary conditions for t=0, q=0, Eq. (5) becomes

$$t/q = 1/(k_2 q_e^2) + t/q_e.$$
 (6)

The rate constant k_2 can be obtained from the intercept of the linearized pseudo-second order rate equation. If the pseudo-second order equation can fit the sorption data, there should be good linearity between t/q and t.

When $t \rightarrow 0$, the initial sorption rate *u* can be defined as

$$u = k_2 q_e^2. \tag{7}$$

Half-adsorption time $(t_{1/2})$ is the time required for the adsorption to take up half as much cobalt as its equilibrium value. This time is an indicator for the adsorption rate. It was calculated from the following equation:

$$t_{1/2} = 1/k_2 q_{\rm e}.$$
 (8)



Fig. 3. (a) linear fit of experimental data obtained using pseudo-first order kinetic model ($\log(q_e - q)$ versus t); (b) linear fit of experimental data obtained using pseudo-second order kinetic model (t/q versus t).

The relationship between $\ln(q_e - q)$ versus time *t* in this work was not linear over the entire time range (Fig. 3(a), $R^2 = 0.926$), indicating that more than one mechanism is involved in adsorption. However, Fig. 3(b) showed that the pseudo-second order equation was ideally applicable to all the sorption data ($R^2 = 0.999$, p < 0.0001). q_e and k_2 obtained by linear regression of t/q against *t* were 17.50 mg g⁻¹ adsorbent and 0.032 g mg⁻¹ min, respectively. The initial sorption rate *u* was 9.8 mg kg⁻¹ min⁻¹ and half-adsorption time was 1.79 min.

3.4. Intraparticle diffusion studies

If the movement of the metal ion from the bulk liquid film surrounding the particle is ignored, the adsorption process can be divided into boundary layer diffusion, sorption of ions to sites and intraparticle diffusion. It is generally accepted that sorption of ions to sites is quite rapid and does not represent the rate determining step. Boundary layer diffusion is characterized by the initial rate of metal ion adsorption. This can be represented by the initial slope of $C_t/C_0 - t$ (C_t , ratio of residual concentration in solution at time t, C_0 , the initial concentration) curves assuming that the relationship over the first 5–10 min is linear [16]. The initial rate of Co(II) ion adsorption to the bone char was 0.235.

Intraparticle diffusion will be the rate limiting step in many cases and can be determined by using following equation [17]:

$$k_{\rm p} = q / t^{1/2}$$
 (9)



Fig. 4. The amount of Co^{2+} adsorbed (*q*) versus square root of time ($t^{1/2}$).

where *q* is the amount of metal adsorbed at time *t*, (mg g⁻¹), k_p the intraparticle rate constant (mg g⁻¹min^{1/2}).

The relationship between *q* and $t^{1/2}$ was not linear over the entire time range (Fig. 4) and the multi-linear plots indicated that two or more steps influence the sorption process. Some researchers [16,18] also reported this non-linear relationship. They considered that there were both boundary diffusion and intraparticle diffusion. Boundary diffusion usually could be represented by the initial curved portion and intraparticle diffusion by the final curved portion. In the present study, cobalt sorption equilibrium was approached at 120 min and little cobalt was adsorbed to bone char from 120 min to 180 min. Intraparticle diffusion seems to be the rate determining step from 45 min to 120 min because there was good linearity over this time range ($R^2 = 0.986$). The rate constant of intraparticle diffusion (k_p), which was calculated from the slope of the final linear portion (from 45 min to 120 min), was 0.157(mg g⁻¹ min^{1/2}).

Theoretically, if the intraparticle diffusion was the only rate determining step, the initial rate parameter (k_i) derived by the slope of linear regression between t = 0 and t_{lim} (the first breakpoint of the curve) should be directly related to $C_0^{1/2}$ [15]. In this study, the k_i was 6.74 and it was far less than $C_0^{1/2}$ (14.14). This confirmed that intraparticle diffusion was not the only rate determining step for Co(II) adsorption by bone char over the entire sorption time range.

3.5. Equilibrium sorption isotherms

The equilibrium of the process was described by Langmuir and Freundlich isotherm models, respectively. The Langmuir isotherm model is a theoretical model for monolayer adsorption:

$$q = q_{\max} bC_e / (1 + bC_e) \tag{10}$$

where *q* is the amount of metal adsorbed, mg g⁻¹ (dry mass); q_{max} is the maximum metal uptake value corresponding to sites saturation, mg g⁻¹(dry mass); C_e is the equilibrium metal concentration in solution, mg L⁻¹; and *b* is the ratio of adsorption/desorption rates.

The Freundlich isotherm model is an experimental model and it is usually expressed as follows:

$$q = kC_{\rm e}^{1/n} \tag{11}$$

where *k* and *n* are constants related to sorption capacity and sorption intensity, other symbols are as previously described.

The sorption data over a concentration range 100–1000 mg L⁻¹ were well represented by the Freundlich isotherm model (Fig. 5(a), $R^2 = 0.9962$). Most of the sorption data, however, did not follow the



Fig. 5. (a) Freundlich adsorption isotherm; (b) Langmuir adsorption isotherm.

Langmuir isotherm model (Fig. 5(b), $R^2 = 0.8668$). Constants of both isotherm models are listed in Table 1. Application of Freundlich model to the equilibrium data of Co(II) indicates the monolayer coverage of bone char by the ion of Co(II) but this was to non-distinct, or multiple, sites of adsorption, unlike the Langmuir model which is to distinct localized adsorption sites [19].

3.6. Influence of competitive cations

In order to study the effect of Cu (II) or Zn (II) on Co (II) adsorption to bone char, Co(II) concentration was kept at a constant value of 200 mg L⁻¹, while the concentrations of Cu (II) or Zn (II) varied from 50 mg L⁻¹ to 250 mg L⁻¹. As shown in Fig. 6, both Cu (II) and Zn (II) ions had an appreciable effect on the cobalt uptake capacity by bone char. When Cu (II) and Co(II) were simultaneously present in the solution, 100% of copper was removed from the solution at an initial Cu (II) concentration from 50 mg L⁻¹ to 250 mg L⁻¹ whereas Co(II) removal percentage

Table 1

Constants for cobalt sorption by bone char with initial cobalt concentration ranged from 100 mg L^{-1} to 1000 mg L^{-1} .

Model	Constants	R^2	SD	Р
Freundlich	$k = 0.1332, 1/n = 0.9088$ $q_{\rm m} = 108.70, b = 0.0542$	0.9962	0.09135	<0.0001
Langmuir		0.8668	0.1257	<0.0001



Fig. 6. Influence of competitive cations (Cu²⁺ or Zn²⁺) on the amount of Co²⁺ adsorbed by bone char.

decreased from 94.20% to 78.26% as the initial Cu (II) concentration increased from 50 mg L⁻¹ to 250 mg L⁻¹. This result indicates that bone char has higher affinity for Cu (II) than Co(II). Similarly, it was also found that bone char had higher affinity for Zn (II) than Co(II). In the binary metal solution including Zn (II) than Co(II), Co(II) removal percentage decreased from 88.42% at an initial Zn(II) concentration of 50 mg L⁻¹ to 74.86% at an initial Zn(II) concentration of 250 mg L⁻¹, whereas 99.95% to 95.85% of Zn (II) in the binary metal solution was adsorbed to bone char as the initial Zn (II) concentration increased from 50 mg L⁻¹. This study showed that the presence of Cu(II) or Zn (II) ions had inhibited cobalt sorption to bone char.

3.7. Mechanisms

The bone char is mainly composed of calcium hydroxyapatite (CaHA), carbon and CaCO₃. Some researchers noted that CaHA is not just a source for adsorption but also enables ion exchange to occur [20,21]. Calcium concentration in solution and XRD analysis showed that ion exchange was involved in removal of Co from solution over a certain initial cobalt concentration range. There was good linear relationship (R^2 = 0.9887) between release of calcium into solution and cobalt adsorbed to bone char over a cobalt concentration range from 10 mg L⁻¹ to 1000 mg L⁻¹ (Fig. 7). However, the calcium released into solution was apparently influenced by the ratio of cobalt



Fig. 7. Calcium released into solution versus the amount of cobalt adsorbed.



Fig. 8. The mole ratio of Ca^{2+} released to Co^{2+} adsorbed versus the mass ratio of cobalt to adsorbent.

to adsorbent (Fig. 8). When the ratio of cobalt to adsorbent was less than 0.03, only part of the cobalt substituted for calcium (Eq. (12)):

$$Ca_{10}(PO_4)_6(OH)_2 + xCo^{2+} \rightarrow Co_yCa_{(10-y)}(PO_4)_6(OH)_2 + yCa^{2+}$$
 (12)

In this work, as the ratio of cobalt to adsorbent increased from 0.001 to 0.02, the ratio of mole calcium released to the mole of cobalt adsorbed increased from 0.037 to 0.8969. When the ratio of cobalt to bone char was greater than 0.3, nearly 1 mol of calcium was released as 1 mol of cobalt was adsorbed, indicating ion exchange was the most predominant mechanism.

$$Ca_{10}(PO_4)6(OH)_2 + 10Co^{2+} \rightarrow Co_{10}(PO_4)6(OH)_2 + 10Ca^{2+}$$
 (13)

Wilson et al. [22] reported that 0.72 mol or 0.2 mol calcium was exchanged for every one mol copper or zinc was adsorbed. The reasons for the differences between different metal sorption are still not clear.



Fig. 9. XRD patterns of bone char before (a) and after (b) incubation with cobalt solutions.

Electronegativity, speciation, ion-size and amount of space in the d-orbitals are considered to have an influence [21,23]. XRD analysis showed that the small peak belonging to CaHA at the left shoulder of the big peaks disappeared after the bone char was incubated in cobalt solution for 3 h and the peak belonging to $Co_{10}(PO_4)6(OH)_2$ appeared (Fig. 9).

The first portion of sorption kinetics indicated that a rapid uptake occurred during the first 5 min. Then, the metal uptake slowly reaches equilibrium. With initial cobalt concentration of 200 mg L⁻¹ the metal removal percentage reaches 75.31%. The cobalt uptake capacity at 5 min was 15.06 mg g⁻¹ and the cobalt uptake capacity at 24 h reached 18.37 mg g⁻¹, indicating that cobalt uptake reaction continued to go on with a very slow rate. Valsami-Jones et al. [24] and Deydier et al. [25] observed similar sorption step in lead sorption to apatite or bone char. On the basis of their explanation, the adsorbent particle was coated with insoluble Co₁₀(PO₄)6(OH)₂ layer that was adsorbed at the earlier stage and it would act as a shield, dramatically decreasing phosphate dissolution rate and consequently Co²⁺ ions uptake. The cobalt uptake step could be explained by slow diffusion of cobalt in the solid, thus making cobalt phosphate an effective barrier.

To sum up, cobalt uptake was very rapid during the first 5 min, substantive calcium in CaHA was exchanged out by cobalt and the cobalt apatite coating was formed. Then slow diffusion of cobalt in the solid went on very slowly during the following long period.

4. Conclusions

Swine bone char is effective in removing cobalt from solution. Batch kinetics studies showed that a rapid uptake occurred within the first 5 min and the metal uptake slowly reaches equilibrium. The kinetics of cobalt sorption by bone char was ideally conformed to pseudo-second equation, indicating several mechanisms are involved in the adsorption process. Equilibrium sorption isotherm studies showed that the Freundlich isotherm model satisfactorily described the sorption data. The presence of co-ions such as copper and zinc had appreciable inhibiting effects on cobalt uptake by bone char because copper and zinc had higher affinity for bone char surface than cobalt. Calcium concentration in solution and XRD analysis showed that ion exchange was involved in the sorption process over a certain initial cobalt concentration range. When the ratio of cobalt to bone char was greater than 0.3, nearly 1 mol of calcium was released as 1 mol of cobalt was adsorbed.

List of symbols

- $q_{\rm e}$ the amount of metal sorbed per unit weight of sorbent at equilibrium, mg g⁻¹ adsorbent;
- *q* the amount of metal sorbed per unit weight of sorbent at time *t*, mg g^{-1} adsorbent;
- k_1 the rate constant of pseudo-first order sorption, l/min;
- k_2 pseudo-second order rate constant, g mg⁻¹ min⁻¹;
- $C_{\rm t}$ ratio of residual concentration in solution at time *t*, mg L⁻¹; C_0 the initial concentration, mg L⁻¹;
- k_p the intraparticle rate constant, mg g⁻¹ min^{1/2};
- $k_{\rm i}$ the initial rate parameter;
- *u* the initial sorption rate;
- *t*_{lim} the first breakpoint of the diffusion curve, min;
- q_{max} the maximum metal uptake value corresponding to sites saturation, mg g⁻¹ dry adsorbent;
- $C_{\rm e}$ the equilibrium metal concentration in solution, mg L⁻¹;
- *b* the ratio of adsorption/desorption rates in Langmuir model;
- *k* rate constants of Freundlich model related to sorption intensity of a sorbent;
- *n* rate constants of Freundlich model related to sorption intensity of a sorbent.
- pH_{pzc} the pH of the point of zero charge

Acknowledgements

This work was supported by Knowledge Innovation Program of Chinese Academy of Sciences (KZCX2-YW-335 and KZCX2-YW-135), Program of 100 Distinguished Young Scientists of the Chinese Academy of Sciences, National Natural Science Foundation of China (40673070, 40872169) and the 863 program project 2006AA06Z339 from Ministry of Science and Technology of the People's Republic of China. We thank two anonymous reviewers for their helpful comments.

References

- A. Kapoor, Viraraghavan, Removal of heavy metals from aqueous solutions using immobilized fungal biomass in continuous mode, Wat. Res. 32 (1998) 1968–1977.
- [2] J. Lewis, The use of bone charcoal in the treatment of rural water supplies, Journal of the Chartered Institute of Water and Environmental Management 9 (1995) 385–395.
- [3] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetics for the removal of copper and zinc from effluents using bone char, Separation Purification Technology 19 (2000) 55–64.
- [4] S. Al-Asheh, N. Abdel-Jabar, F. Banat, Packed-bed sorption of copper using spent animal bones: factorial experimental design, desorption and column regeneration, Advances in Environmental Research 6 (2002) 221–227.
- [5] C.K. Danny, C.W. Cheung, K.H. Keith, G. Mckay, Sorption equilibria of metal ions on bone char, Chemosphere 54 (2004) 273–281.
- [6] K.H. Keith, C.K. Danny, C.W. Cheung, Film and intraparticle mass transfer during the adsorption of metal ions onto bone char, Journal of Colloid and Interface Science 271 (2004) 284–295.
- [7] M.W. Abdel Raouf, A.A.M. Daifullah, Potential use of bone charcoal in the removal of antimony and europium radioisotopes from radioactive wastes, Ads. Sci. Technol. 15 (1997) 559–569.
- [8] Y.N. Chen, L.Y. Chai, Y.D. Shu, Study of arsenic(V) adsorption on bone char from aqueous solution, J. Hazard. Mater 160 (2008) 168–172.
- [9] Y. Xu, Sorption of zinc and cadmium on hydroxyapatite surfaces, Environmental Science and Technology 28 (1994) 1472–1480.
- [10] J.W. Moore (Ed.), Inorganic contaminants of surface water residuals and monitoring priorities, Springer-Verlag, New York, 1994, pp. 178–210.
- [11] S.D. Lambert, N.J.D. Graham, Adsorption methods for treating organically coloured upland waters, Envir. Tech. Lett. 10 (1989) 785–798.
- [12] L. Wu, W. Forsling, P.W. Schindler, Surface complexation of calcium minerals in aqueous solutions. 1. Surface protonation of fluoroapatite water interfaces, J. Colloid Interface Sci. 147 (1991) 178–185.
- [13] I. Smičiklas, S. Milonjić, P. Pfendt, S. Raičević, The point of zero charge and sorption of cadmium (II) and strontium (II) ions on synthetic hydroxyapatite, Sep. Purif. Technol. 18 (2000) 185–194.
- [14] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (1898) 1–39.
- [15] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
- [16] O. Keskinkan, M.Z.L. Goksu, M. Basibuyuk, C.F. Forster, Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*), Bioresource Technology 92 (2004) 197–200.
- [17] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Engng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.
- [18] N. Fernandez, C. Chacin, C. Garcia, The use of seed pods from Albizia lebbek for the removal of alkyl benzene sulphonates from aqueous solution, Process Biochem. 32 (1996) 383–387.
- [19] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solutions by the fly ash, Water Res. 19 (1985) 869–873.
- [20] T. Suzuki, T. Hatsushika, Y. Hayakawa, Synthetic hydroxyapatite employed as inorganic cation-exchanger, J. Chem. Soc. (Faraday Transaction I) 77 (1981) 1059–1062.
 [21] Y. Takeuchi, H. Arai, Removal of coexisting Pb²⁺, Cu²⁺ and Cd²⁺ ions from water
- [21] Y. Takeuchi, H. Arai, Removal of coexisting Pb²⁺, Cu²⁺ and Cd²⁺ ions from water by addition of hydroxyapatite powder, J. Chem. Eng. Jpn. 23 (1990) 75–80.
- [22] J.A. Wilson, I.D. Pulford, Thomas, Sorption of Cu and Zn by bone charcoal, Environmental Geochemistry and Health 25 (2003) 51–56.
- [23] M.W.A. Raouf, A.A.M. Daifullah, Potential use of bone charcoal in the removal of antimony and europium radioisotopes from radioactive wastes, Adsorption Science and Technology 15 (1997) 559–569.
- [24] E. Valsami-Jones, K.V. Ragnarsdottir, D.A. Putnis, The dissolution of apatite in the presence of aqueous metal cations at pH 2–7, Chem. Geol. 151 (1998) 215–233.
- [25] E. Deydier, R. Guilet, P. Sharrock, Beneficial use of meat and bone meal combustion residue: an efficient low cost material to remove lead from aqueous effluent, Journal of Hazardous Materials 101 (2003) 55–64.