Facilitated desorption and stabilization of sediment-bound Pb and Cd in the presence of birnessite and apatite

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ABSTRACT

Desorption of lead (Pb) and cadmium (Cd) from contaminated sediments was investigated to clarify the effect of stabilizing agents on Cd and Pb desorption kinetics. The desorbed aqueous Cd and Pb concentrations and the residual amounts of Cd on the sediments in the desorption tests were best fitted to a pseudo-second-order kinetics with the highest R^2 values among the models used in the kinetic studies. The average residual Cd on sediments were 24% and 19% less in the presence of apatite and birnessite, respectively, than in the absence of them. However, the Pb desorption was not affected by the stabilizing agents. The negligible aqueous concentrations of desorbed Cd and Pb in the presence of apatite and birnessite suggest the stabilization of desorbed Cd that was facilitated by apatite and birnessite and Pb. The kinetics study with Cd shows that the rate constants are not affected, but the desorption extents are affected in the presence of apatite and birnessite. The Tessier sequential extraction method and toxicity characteristic leaching procedure indicate that Pb is more strongly bound on the stabilizing agents than Cd. Overall, birnessite and apatite can be successfully applied in remediation of Cd and Pb contaminated sediment.

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1. Introduction

Heavy metals desorption from heavy metals contaminated sediment to an aqueous phase depends on factors such as pH, redox potential, organic matters, temperature, ionic strength, mixing, and time [1,2]. The desorbed heavy metals can pose direct harm to aqueous organisms and human health and could become a secondary pollution source [3]. Among heavy metals, cadmium (Cd) and lead (Pb) became ubiquitous pollutants in the environment due to wide spread use and they are included on the US Environmental Protection Agency's (EPA) list of priority pollutants [4]. They tend to adsorb on sediments once they are released into waterways. Heavy metals in the resulting contaminated sediments can be resuspended and dissolved into the overlying water or ingested by small organisms living on the bottom of water and bioaccumulate in organisms in the higher levels of the food chain [5,6]. The remediation techniques for heavy metal contaminated soils such as washing, thermal extraction, bioremediation, electrolytic processes, stabilization, and chemical oxidation may not be as efficient for the remediation of contaminated sediments and, generally, contaminated sediments are dredged and, after pretreatment and physical separation, contained in confined disposal facilities due to

the difficulties and high costs with desorbing heavy metals from fine sediments [7].

Stabilization of heavy metals is one of the contaminated sediment remediation techniques that aims at minimizing toxic effects of heavy metals that could be released from contaminated sediments using stabilizing agents. Heavy metal stabilization has been receiving increasing attention as a mean of reducing mobility, bioavailability, and toxicity of heavy metals. The mobility of desorbed heavy metals in contaminated sediments is reduced by sorbing on stabilizing agents added [8]. Various stabilizing agents such as zeolite, ferrihydrite, and apatite, individually or in combination, have been used in heavy metal stabilization studies and these studies mainly investigated the effect of stabilizing agents on heavy metals distribution and the bioavailability of heavy metals in sediments [9–11].

There are different models available for analyzing desorption processes such as pseudo-first-order model, pseudo-second-order model, Elovich model, parabolic diffusion model, and power function. Previous kinetic studies investigated desorption of metals in contaminated soils and sediments to an aqueous phase and adsorption of dissolved metals in an aqueous phase on stabilizing agents separately [12–14]. While the stabilization process involves both desorption of metals in sediments and adsorption of metals on stabilizing agents, these two processes have not been studied together in one system as desorption and adsorption processes could not be studied separately due to the difficulty in separating sediment particles and stabilizing agent particles. Therefore, this investigation

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was undertaken to study whether the presence of apatite or bir-nessite with contaminated sediments drives desorption of Cd or Pb in sediments to promote stabilization process of the contaminated sediments. Particularly, existing kinetic models were used to fit the desorption data to account for the effects of apatite or birnessite on desorption of Cd or Pb in sediments.

2. Materials and method

2.1. Sediment preparation

Sediment collected from the Kyeong-an creek, a tributary to the Han River in South Korea, was air-dried and passed through a 200-mesh sieve to remove particles larger than 0.074 mm. The organic carbon content of the sediment, cation exchange capacity (CEC), and pH were 1.21%, 11.70 cmol kg^{-1}, and 6.20, respectively [15]. The sediment consists mainly of sand (75.0%) with silt (14.7%) and clay (10.3%). The background concentrations of Cd, Pb, Cr, As, and Hg in the sediment determined following the EPA Method 3050B were 0.54 mg kg^{-1} Cd, 22.9 mg kg^{-1} Pb, 54.3 mg kg^{-1} Cr, 6.69 mg kg^{-1} As, and 0.03 mg kg^{-1} Hg.

Contaminated sediments were prepared by placing sediment in vessels with 5 mM Cd or Pb ion solution at room temperature and the vessels were mixed intermittently. After 7 d the supernatant was removed and contaminant-free deionized water was added to wash the sediments and then the sediments were air-dried. The resulting sorbed concentrations were 1675 ± 173 mg kg^{-1} for Cd and 2257 ± 176 mg kg^{-1} for Pb. The background Cd and Pb concen-trations in the sediment were not considered since the background concentrations were only 0.03% and 1.0% of the sorbed concentra-tions of Cd and Pb, respectively.

2.2. Solutions and chemicals

Solutions of Cd and Pb were prepared from cadmium chlo-ride 2.5-hydrate (CdCl$_2$ 2.5H$_2$O, >98.8%, Kanto Chemical Co., Japan) and lead(II) chloride (PbCl$_2$, 99.0%, Junsei Chemicals Co., Japan) powders, respectively. All solutions were prepared with ultrapure deionized water (Milli-Q, Millipore, US). Since Cd is known to be mobile at pH values between 4.5 and 5.5 [5], the pH values of metal solutions and water used for experiments were adjusted to 5.2 ± 0.1 with 1 N NaOH or 1 N HNO$_3$. Apatite (calcium phosphate triba-sic) was purchased from Sigma (US) and birnessite was prepared according to procedures outlined by McKenzie [16].

2.3. Desorption/adsorption experiments

The Cd or Pb desorption experiments in sediments were carried out with 5.2 ± 0.1 g of Pb- or Cd-contaminated sediment and 20 mL of the pH adjusted water (pH 5.0 ± 0.1). The adsorption experiments of Cd or Pb onto apatite and birnessite were performed with 0.25 g apatite or birnessite and 20 mL of pH adjusted Pb or Cd solutions at 1 and 30 mM (207 and 6210 mg L^{-1} for Pb and 112 and 3360 mg L^{-1} for Cd) to explore the stabilization effects of apatite and birnessite. For each experiment, triplicate samples were prepared in 50 mL centrifuge tubes and the samples were placed on a reciprocating mixer (80–100 rpm) during the reaction period. At pre-determined times, samples were vacuum filtered and diluted accordingly for analyses.

To study the desorption kinetics of Cd or Pb in the stabilization process where desorption and adsorption occur together in one reactor, the contaminated sediments were placed in bags made from dialysis tubing cellulose membranes (MW 12.4 kD) (Sigma, US), which were used to keep the sediment separate from apatite or birnessite to measure the residual amounts of Pb or Cd on the sediments and to slow down the initial desorption process. Apatite
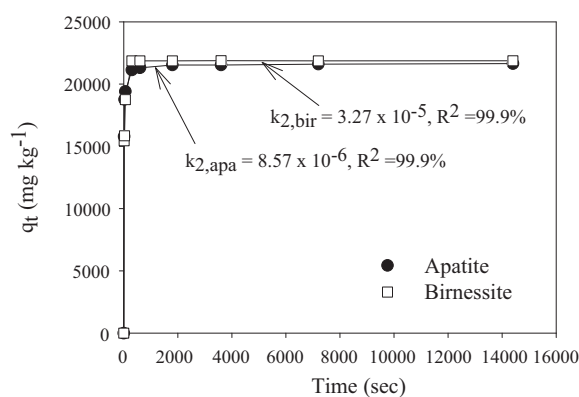

Fig. 1. Adsorption of cadmium (Cd) in an aqueous solution on apatite and birnes-site. pH = 5.0 ± 0.5, T = 22 ± 1 °C, Cd solution concentration = 112 mg L^{-1}, Cd solution volume = 20 mL, mass of apatite or birnessite = 0.25 g.

or birnessite was placed in tubes together with the sediment bags. Samples without stabilizing agents were used as controls. The residual amount of Cd and Pb on sediments in the absence and presence of apatite and birnessite were analyzed to study whether desorption is facilitated by apatite and birnessite and the aqueous Cd and Pb concentrations were analyzed to see whether apatite and birnessite can satisfactorily adsorb the desorbed Cd and Pb.

2.4. Analytical methods

The aqueous Pb and Cd concentrations were determined using flame atomic absorption spectrometry (FLAA) (AA7000, Shimadzu, Japan) with the method detection limits of 0.003 mg L^{-1} for Cd and 0.059 mg L^{-1} for Pb. The relative standard deviation (RSD) of three replicate analyses was generally below 5%. The solid phase Pb and Cd were extracted by US EPA Method 3052 microwave digestion method [17] and analyzed using FLAA. All results were expressed as an average of triplicate samples.

A Tessier sequential extraction method [18] and toxicity char-acteristic leaching procedure (TCLP) described in US EPA SW-846 Method 1311 [19] were used to evaluate stabilization effects of bir-nessite and apatite (i.e., how strongly Cd and Pb are adsorbed on birnessite and apatite) on heavy metal distribution after carrying out the Cd and Pb adsorption experiments using 1 or 30 mM Cd or Pb solutions.

3. Results and discussion

3.1. Adsorption and desorption of Cd and Pb

The Langmuir isotherm model was used to describe the sorp-tion isotherm of Cd and Pb in aqueous solutions on apatite and birnessite with $0.96 < R^2 \leq 1.00$ [11]. The evaluated sorption capaci-ties of apatite were 2.22×10^5 and 1.33×10^5 mg kg^{-1}, respectively, for Pb and Cd and the evaluated sorption capacities of birnessite were 3.62×10^5 and 1.22×10^5 mg kg^{-1} for Pb and Cd, respec-tively. These capacities were in the same order of magnitude with the previous study using nano-hydroxyapatite (4.16×10^5 and 1.58×10^5 mg kg^{-1} for Pb and Cd, respectively) [11].

With aqueous Cd solution, the adsorption of Cd on apatite and birnessite happened very quickly (Fig. 1) and the possibility of such quick reactions promoting Cd or Pb desorption in sediments was studied with the contaminated sediment in dialysis membrane bags. In the absence of stabilizing agents, the dialysis membranes delayed Cd and Pb desorption from the contaminated sediments enabling the observation of the desorption behavior during the ini-tial desorption period. Within the first 30 min of the 3 d desorption
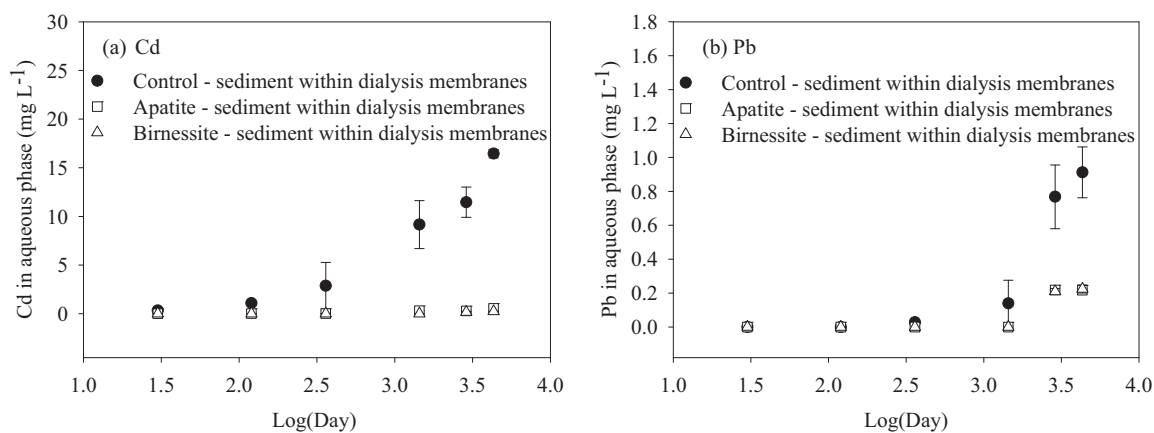
Fig. 2. Amount of desorbed (a) Cd and (b) Pb in aqueous phases. The Cd- or Pb-contaminated sediment was placed in dialysis membranes. With samples with apatite and birnessite, 5% (w/w) apatite and birnessite were used, respectively. pH = 5.0 ± 0.5, T = 22 ± 1 °C, sediment = 5.00 ± 0.05 g, pH adjusted water = 20 mL.

period, the contaminated sediments released, on average, 63 and 44% of the maximum amounts of Cd and Pb released while the contaminated sediments in the dialysis membrane only released, on average, 2 and 0% of the maximum amounts of Cd and Pb released. This can be attributed to the combined effects of the time taken for water to diffuse in and wet the sediment inside the membranes and the controlled diffusion of the desorbed Cd or Pb through the membranes to aqueous phases.

The initial solution pH values were 5.2 ± 0.1 and the final pH values were 5.8 ± 0.1 in the presence of the contaminated sediments. The final pH values were 6.3 ± 0.1 and 6.4 ± 0.1 in the presence of apatite and birnessite, respectively.

3.2. Desorption kinetic studies using aqueous Cd and Pb concentrations

Fig. 2 shows the Cd and Pb desorption from the contaminated sediments in the dialysis membranes. With the Cd-contaminated sediment, while the aqueous Cd concentrations in the controls continued to increase for the 3 d desorption period, the aqueous Cd concentrations in the samples with apatite and birnessite were only 3.4 and 1.4% of the maximum amount of Cd released in the controls, respectively, after 3 d (Fig. 2a). Similarly, the aqueous Pb concentration continued to increase for 3 d in the controls, but the aqueous Pb concentrations in the presence of apatite and birnessite were 24 and 25% of the maximum amount of Pb released in the controls, respectively (Fig. 2b). The relatively lower aqueous Cd and Pb concentrations in the presence of apatite and birnessite suggest the adsorption of Cd and Pb on apatite and birnessite. The significantly lower concentration ranges of Pb than Cd under the same conditions can be attributed to the higher affinity of Pb than Cd [20].

In the absence of apatite and birnessite, the Cd and Pb desorption shows a good linear fit to a linearized form of a pseudo-second-order equation (Fig. 3) with the higher coefficient of determination (R^2) values ($R^2 > 1.00$ for Cd and $R^2 > 0.99$ for Pb) than other models such as pseudo-first-order equations ($R^2 > 0.58$ for Cd and $R^2 > 0.01$ for Pb), Elovich model ($R^2 > 0.61$ for Cd and $R^2 > 0.47$ for Pb), and power function ($R^2 > 0.63$ for Cd and $R^2 > 0.48$ for Pb).

3.3. Residual amounts of Cd and Pb on the contaminated sediments after desorption

The residual Cd and Pb left on the Cd- and Pb-contaminated sediments were extracted to observe the effect of apatite and bir-

nesstie on the desorption extent of Cd and Pb in the contaminated sediments. Fig. 4 shows the changes in the residual amounts of Cd and Pb left on the sediments. With the controls in the absence of stabilizing agent, the amounts of Cd and Pb left on the sediments after 3 d desorption period were 76 and 98% of the initially sorbed amounts of Cd and Pb, respectively. In the presence of apatite and birnessite, the average amounts of Cd left on the sediment were 24 and 11% lower than the amounts of Cd left in the controls, respectively. As seen in Fig. 4(a) and (b), while the Cd desorption was greater in the presence of apatite, the Cd desorption in the pres-
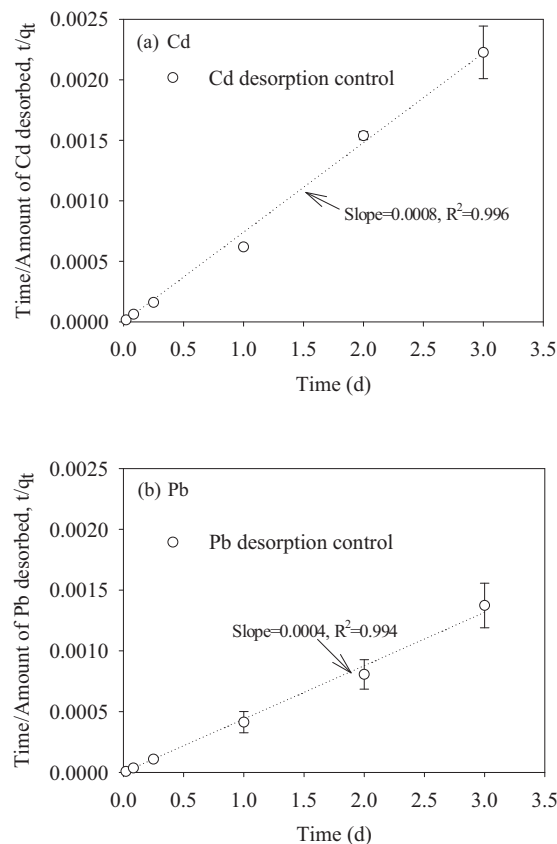

Fig. 3. Desorption of (a) Cd in the Cd-contaminated sediment and (b) Pb in the Pb-contaminated sediment fitted to a linearized form of a pseudo-second-order equation. The sediments were placed in dialysis membranes. Initial pH = 5.0 ± 0.5, T = 22 ± 1 °C, sediment = 5.00 ± 0.05 g, pH adjusted water = 20 mL.
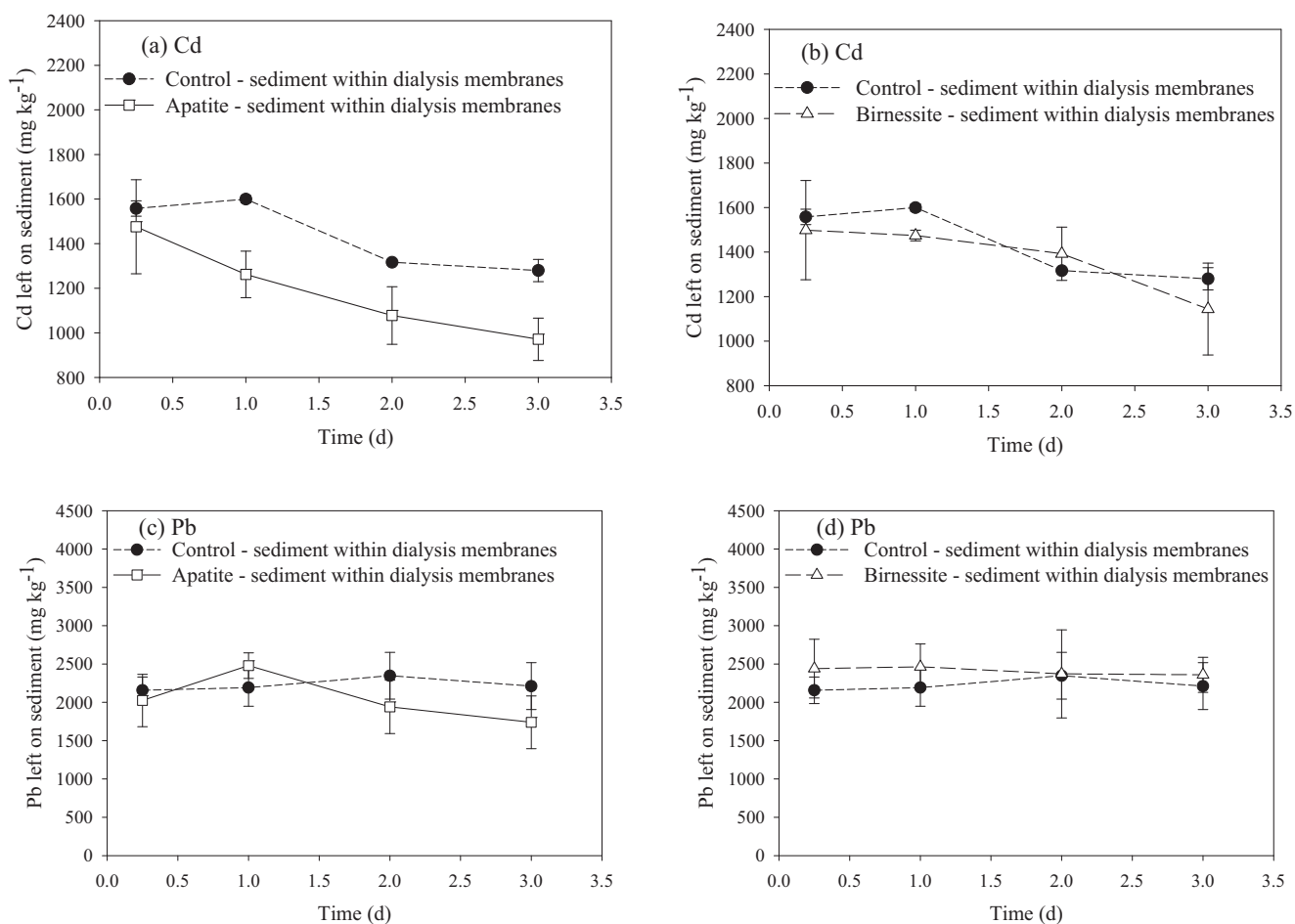
Fig. 4. Residual (a) Cd in the presence of apatite (b) Cd in the presence of birnessite (c) Pb in the presence of apatite and (d) Pb in the presence of birnessite on the sediments during the desorption experiments. pH = 5.0 ± 0.5, T = 22 ± 1 °C, sediment in dialysis membranes = 5.00 ± 0.05 g, water = 20 mL. apatite/birnessite = 5% (w/w).

ence of birnessite was statistically similar to that of the controls. With Pb, the amounts of Pb left on the sediment were statistically similar to that of the controls (Fig. 4(c) and (d)). The results show that Cd desorption in sediments is promoted in the presence of apatite, but not in the presence of birnessite. The lower facilitation effects of apatite and birnessite for Pb than Cd can be attributed to the higher affinity of Pb than Cd [20].

The changes in the residual amounts of Cd on the Cd-contaminated sediment (i.e., decrease in the amount of the Cd adsorbed on the sediment) were fitted to the pseudo-first-order equation, the pseudo-second-order equation, the Elovich model, and the Power function. The suitability of each model to fit the residual Cd data was evaluated by obtaining the R^2 values from linear regression analysis of the residual Cd data. The residual Cd data was fitted best to the pseudo-second-order equation, as indicated by the higher R^2 values ($0.983 \leq R^2 \leq 0.996$) (Fig. 5). The ranges of the R^2 values were 0.545–0.666 for the pseudo-first-order model, 0.007–0.957 for the Elovich model, and 0.013–0.949 for the power function.

The time/residual Cd on sediment data show a good linear fit to time and a positive slope corresponds to a decrease in the residual Cd with increasing time (Fig. 5). The estimated values of the residual Cd left on the sediment at equilibrium, q_e, and the rate constant describing the reduction in the residual Cd left on the sediment with time, k_2, are shown in Table 1. The q_e values in the presence of apatite and birnessite were smaller than the q_e value for the controls. The estimated k_2 values were negative indicating decreases in the residual Cd on the sediments. The k_2 values
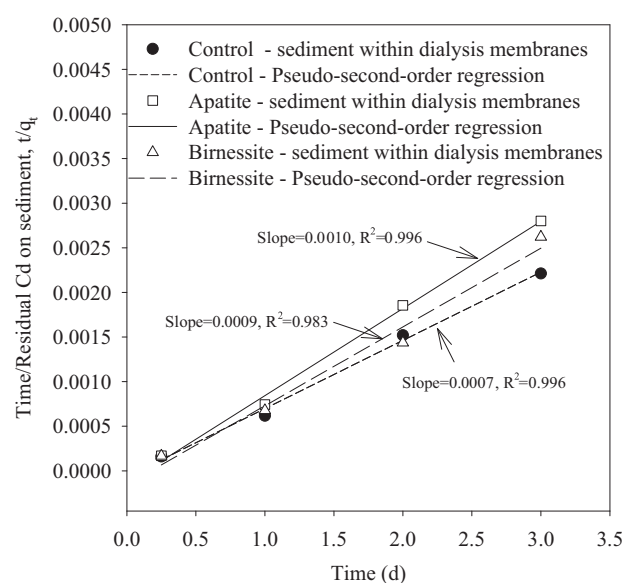

Fig. 5. Kinetics analysis of residual cadmium on the contaminated sediment after 3 d desorption experiment by linear plots of pseudo-second-order rate equations.

for the samples with apatite or birnessite and the controls were in the similar magnitude indicating that the rate at which the residual Cd on the sediment decreases is similar in the absence and the presence of apatite and birnessite. These results show that while

Table 1
Comparison of parameters of the pseudo-second-order equations describing the reduction in the amount of cadmium left on the contaminated sediment during the desorption process.

Parameter	Control	Apatite	Birnessite
k_2 (mg kg^{-1} d^{-1})	−0.008	−0.007	−0.005
q_e (mg kg^{-1})	1359	1024	1132
R^2	0.996	0.996	0.983

the presence of apatite facilitates the Cd desorption, the rate constants are not significantly affected by the presence of apatite and birnessite.

3.4. Comparison of the extractability of Cd and Pb adsorbed on sediments and apatite or birnessite

Whether or not desorption of Cd and Pb is facilitated by the apatite or birnessite, the desorbed Cd and Pb stabilizes on apatite and birnessite. Thus, the stabilization efficiency of Cd and Pb by birnessite and apatite was investigated using the TCLP and the Tessier Sequential extraction method to confirm that the stabilized Cd and Pb on apatite and birnessite do not harm the aqueous systems with contaminated sediments. With the Tessier Sequential extraction method, the five fractions in the Tessier Sequential extraction method were grouped into non-specific sorption fraction (exchangeable and organic-bound fractions) representing weak sorption and specific sorption fraction (carbonate-bound, oxide-bound, and residual fractions) representing high binding strength [21]. The non-specific sorption fractions were 28%, 71%, and >90% for birnessite, apatite, and sediments, respectively. The TCLP leachate Cd concentration was lower than the Code of Federal Regulations (CFR) of 1 mg L^{-1} with birnessite and apatite sorbed with 1 mM (112 mg L^{-1}) Cd solution. With birnessite and apatite sorbed with 30 mM (3360 mg L^{-1}) Cd solution, while the leachate Cd concentration with birnessite was lower than the CFR, it was greater than the CFR with apatite.

With Pb, the non-specific sorption fractions were <1% with both birnesstie and apatite, while with the sediments, about 85% were non-specific fractions. Pb was not detected in the TCLP leachate from birnessite and apatite sorbed with 1 mM (207 mg L^{-1}) Pb solution. With birnessite and apatite sorbed with 30 mM (6210 mg L^{-1}) Pb solution, 3.3 mg L^{-1} and 0.6 mg L^{-1} of Pb were detected in the leachate, respectively, but these values were still lower than the CFR of 5 mg L^{-1}.

These results indicate that the desorbed Cd and Pb in sediments are stabilized on apatite and birnessite and Pb is more strongly bound on apatite and birnessite than Cd, which can be attributed to the higher affinity of Pb than Cd [20]. With Cd stabilization, birnessite is more effective than apatite and it could be attributed to the different sorption mechanisms used by apatite and birnessite. While Cd is sorbed by surface complexation on birnessite [22], Cd adsorbs on hydroxyapatite via ion exchange and surface complex mechanisms [23,24]. These differences could possibly explain the Cd desorption facilitated by the presence of apatite, but not significantly by birnessite.

4. Conclusions

The facilitation of Cd desorption from the contaminated sediments in the presence of apatite was confirmed using the aqueous Cd concentrations and the residual amounts of Cd on the contaminated sediment. However, Cd desorption in the presence of birnessite and Pb desorption in the presence of apatite and birnessite were similar to that in the absence of apatite and bir-

nessite. The negligible aqueous concentration of desorbed Cd and Pb throughout the desorption period in the presence of apatite and birnessite indicate that they are stabilized on apatite and birnessite after desorption from the sediments. The kinetic studies show that while the Cd desorption extent was enhanced by the presence of apatite, the rate constant was not affected by the presence of stabilizing agents. In addition to these results, the extraction tests results of Cd and Pb from apatite and birnessite suggest that birnessite and apatite can be successfully applied in remediation of heavy metals contaminated sediment. Overall, this study suggests that Cd stabilization with apatite is beneficial as the extent of the Cd desorption in sediment can be enhanced.

Acknowledgements

References

[1] C.W. Gray, R.G. McLaren, A.H.C. Roberts, L.M. Condron, Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time, Aust. J. Soil Res. 36 (1998) 199–216.

[2] S.M. Garman, M.J. Eick, M. Beck, Desorption kinetics of lead from goethite: effect of residence time and mixing, Soil Sci. 172 (2007) 177–188.

[3] S.L. Huang, Z.H. Wan, Present state of experimental research on heavy metal pollutant adsorption–desorption by sediment, Int. J. Sediment. Res. 10 (1995) 69–81.

[4] R.E. Cameron, Guide to Site and Soil Description for Hazardous Waste Site Characterization. Vol. 1: Metals, US Environemntal Protection Agency, Washington, 1992.

[5] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Remediation technologies for metal-contaminated soils and groundwater: an evaluation, Eng. Geol. 60 (2001) 193–207.

[6] C.N. Mulligan, R.N. Yong, B.F. Gibbs, An evaluation of technologies for the heavy metal remediation of dredged sediments, J. Hazard. Mater. 85 (2001) 145–163.

[7] U.S. Environmental Protection Agency, ARCS Remediation Guidance Document, Great Lakes National Program Office, Chicago, US, 1994.

[8] D.L.P.D. Sparks, Environmental Soil Chemistry, Academic Press, San Diego, 1995.

[9] J.f. Peng, Y. h. Song, P. Yuan, X.y. Cui, G.l. Qiu, The remediation of heavy metals contaminated sediment, J. Hazard. Mater. 161 (2009) 633–640.

[10] G. Qian, W. Chen, T.T. Lim, P. Chui, In-situ stabilization of Pb, Zn, Cu, Cd and Ni in the multi-contaminated sediments with ferrihydrite and apatite composite additives, J. Hazard. Mater. 170 (2009) 1093–1100.

[11] Z. Zhang, M. Li, W. Chen, S. Zhu, N. Liu, L. Zhu, Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite, Environ. Pollut. 158 (2010) 514–519.

[12] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[13] G.S.R. Krishnamurti, G. Cieslinski, P.M. Huang, K.C.J. Van Rees, Kinetics of cadmium release from soils as influenced by organic acids: implication in cadmium availability, J. Environ. Qual. 26 (1997) 271–277.

[14] B.W. Strobel, H.C.B. Hansen, O.K. Borggaard, M.K. Andersen, K. Raulund-Rasmussen, Cadmium and copper release kinetics in relation to afforestation of cultivated soil, Geochem. Cosmochim. Acta 65 (2001) 1233–1242.

[15] R. Swift, D. Sparks, Methods of Soil Analysis: Part 3. Chemical Methods, Soil Science Society of America Inc., Madison, WI, USA, 1996.

[16] R.M. McKenzie, The sysnthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese, Miner. Mag. 38 (1971) 493–502.

[17] US EPA Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, Last accessed on 8 June 2010, http://www.epa.gov/wastes/hazard/test methods/sw846/pdfs/3052.pdf, 1996.

[18] A. Tessier, P.G.C. Campbell, M. Blsson, Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51 (1979) 844–851.

[19] US EPA Toxicity Characteristic Leaching Procedure, last accessed on 22 July 2010, http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/1311.pdf, 1992.

[20] E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang, Comparison of sorption of Pb^{2+} and Cd^{2+} on Kaolinite clay and polyvinyl alcohol-modified Kaolinite clay, Adsorption 14 (2008) 791–803.

[21] D.C.W. Tsang, I.M.C. Lo, Competitive Cu and Cd sorption and transport in soils: a combined batch kinetics, column, and sequential extraction study, Environ. Sci. Technol. 40 (2006) 6655–6661.

[22] C.J. Matocha, E.J. Elzinga, D.L. Sparks, Reactivity of Pb(II) at the Mn(III,IV) (oxyhydr)oxide–water interface, Environ. Sci. Technol. 35 (2001) 2967–2972.

[23] R. Zhu, R. Yu, J. Yao, D. Mao, C. Xing, D. Wang, Removal of Cd^{2+} from aqueous solutions by hydroxyapatite, Catal. Today 139 (2008) 94–99.

[24] M. Srinivasan, C. Ferraris, T. White, Cadmium and lead ion capture with three dimensionally ordered macroporous hydroxyapatite, Environ. Sci. Technol. 40 (2006) 7054–7059.