



Simultaneous removal of phenanthrene and lead from artificially contaminated soils with glycine- β -cyclodextrin

Guanghai Wang^{a,*}, Yueming Zhou^a, Xuegang Wang^a, Xinjun Chai^a, Lei Huang^a, Nansheng Deng^b

^a Department of Civil and Environmental Engineering, East China Institute of Technology, Fuzhou 344000, Jiangxi, PR China

^b School of Resources and Environmental Science, Wuhan University, Wuhan 430079, Hubei, PR China

ARTICLE INFO

Article history:

Received 10 February 2010

Received in revised form 24 July 2010

Accepted 20 August 2010

Available online 27 August 2010

Keywords:

Phenanthrene

Lead

Glycine- β -cyclodextrin

Remediation

Co-contaminated soil

ABSTRACT

Preparation of glycine- β -cyclodextrin (GCD) was carried out by the reaction of β -cyclodextrin with glycine in the presence of KOH and epichlorohydrin. The enhanced solubilization behavior of phenanthrene and lead carbonate by GCD was studied, and the desorption behavior of phenanthrene and lead from co-contaminated soil was also investigated. The results showed that GCD has obvious solubilization for phenanthrene and lead carbonate. The solubility of phenanthrene in 30 g/L of GCD was enhanced about 30-fold. And the apparent aqueous solubilities of lead carbonate are also obviously increased with increasing GCD concentration, when the concentration of GCD reached 20 g/L, the aqueous lead concentration was 2945 mg/L. GCD could simultaneously increase the apparent aqueous solubility of phenanthrene and complex with lead. The desorption process of GCD for phenanthrene and lead from co-contaminated soil followed the pseudo-second-order kinetic model. The removal efficiencies of phenanthrene and lead in soil increased dramatically with increasing GCD concentrations. At concentration of 40 g/L, GCD has a removal efficiency of 85.8% and 78.8% for lead and phenanthrene, respectively, from the combined contaminated soil. The use of GCD as an extractant to enhance the removal of heavy and hydrophobic organic contaminants (HOCs) from co-contaminated soils appears as a promising remediation method.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Heavy metals and hydrophobic organic contaminants (HOCs) have been frequently found together in contaminated soils [1,2]. The co-contamination of soils caused by heavy metals and HOCs attracts great concern in recent years due to the high toxicity for plants and animals [3,4]. Thus, the remediation of co-contaminated soil is an important environmental issue, the development of improved and effective remediation technologies for soils contaminated by heavy metals as well as HOCs have emerged as a significant environmental priority. However, to the best knowledge of the authors, most studies on this technique have focused on soils contaminated by a single type of pollutant (i.e., either heavy metals or organic contaminants), whereas there are only a few studies on the simultaneous removal of heavy metals and HOCs from the co-contaminated soils [5–8].

Recently, cyclodextrins (CDs) have received increasing attention because of their forming inclusion complex with various guest molecules with suitable polarity and dimension. There-

fore, they have been proposed as an alternative agent to enhance water-solubility of hydrophobic compounds [9,10]. However, β -cyclodextrin cannot complex metal ions, thus, modified β -cyclodextrin with coordination for metal ions was prepared, for example, some studies have shown that that carboxymethyl- β -cyclodextrin (CMCD) has the ability to complex heavy metals such as cadmium, nickel, strontium and mercury in the presence of various organic contaminants [11–13]. The ability of modified cyclodextrins to increase the apparent solubility of organic and metal compounds is the basis for exploitation in soil remediation. In addition, cyclodextrins present several advantages over solvents and surfactants because of their non-toxicity, higher biodegradability and low affinity of sorption to the solid phase at a wide range of pH values [11,14,15].

In this work, in order to improve the solubilization capacity of β -cyclodextrin for HOCs and insoluble heavy metal salt, a novel modified β -cyclodextrin, glycine- β -cyclodextrin was synthesized by the reaction of β -cyclodextrin with glycine in the presence of KOH and epichlorohydrin, which can be used for the simultaneous removal of organic pollutants and heavy metals from co-contaminated soils. The enhanced solubilization behavior of phenanthrene and lead carbonate by GCD was studied, and the desorption behavior of phenanthrene and lead from co-contaminated soil was also investigated. This research will provide valuable infor-

* Corresponding author. Tel.: +86 794 8258287; fax: +86 794 8258828.
E-mail address: wgh68611@163.com (G. Wang).

mation for the remediation of co-contaminated soil caused by heavy metals and HOCs.

2. Materials and methods

2.1. Materials

β -CD was obtained from Seebio Biotechnology Inc. (Shanghai, PR China), and used without further purification. Phenanthrene was selected as a representative polycyclic aromatic hydrocarbon (PAH) to model the hydrophobic organic contaminants, it was purchased from Jingchun Chemical Reagent Co. (Shanghai, PR China), with a purity of 99%. Glycine, lead carbonate and lead nitrate were analytical pure, also purchased from Jingchun Chemical Reagent Co. (Shanghai, PR China). Epichlorohydrin was obtained from Fuchen Chemical Reagent Co. (Tianjing, PR China). HNO_3 and NaOH were used to adjust the pH values of solutions. All other reagents and solvents used were of analytical reagent grade unless otherwise stated. The water used throughout the work was deionised by a Milli-Q Water Purification system.

2.2. Soil characteristics and preparation of contaminated soil

An uncontaminated natural soil was collected from Fuzhou City, China, the soil was air-dried and sieved to obtain particles less than 2 mm in all experiments. The soil has a pH of 6.80 and organic carbon content of 1.82%. Preparation of co-contaminated soil was carried out as follows: firstly, the Pb-contaminated soil was prepared by completely mixing clean soils with $\text{Pb}(\text{NO}_3)_2$ solution, the soils were air-dried at room temperature for a week. Secondly, phenanthrene was initially dissolved in hexane, and then phenanthrene solution was mixed with above Pb-contaminated soils, the mixture was then ventilated in a fume hood for 8 d to stabilize the contaminated soil (it is uncertain if the phenanthrene in soil is in a sorbed or precipitated state). The contaminated soils have a final concentration of 0.157 and 2.12 mg/g of phenanthrene and lead on mixed contaminated soil, respectively.

2.3. Analytical methods

The UV absorbance spectra of phenanthrene solution were recorded with spectrophotometer UV-1601 (Shimadzu, Japan). The characteristic absorbance peak was at 254 nm. Fluorescence spectra of phenanthrene and its inclusion complex in aqueous solutions were recorded with a Hitachi F-4500FL fluorescence spectrophotometer (Tokyo, Japan), the fluorescence intensity was measured in a 1 cm quartz cell. Excitation wavelength used was set at 249 nm. Phenanthrene in aqueous solution was determined by HPLC [Shimadzu LC-10ATVP pump, Shim-pack VP-DDS-C18 column (4.6 mm \times 150 mm, 5 μm)] with a flow rate of 1.0 mL min^{-1} and UV detector (Shimadzu UV-Vis detector) at 254 nm. The mobile phase was methanol/water mixture (90/10, v/v). The injection volume was 20 μL . The retention time of phenanthrene was about 5.0 min. The concentrations of lead in aqueous solution were measured by a Perkin-Elmer analyst 700 atomic absorption spectrophotometer (AAS). Measurements were made in triplicate in each experiment with errors less than 5%.

2.4. Preparation of glycine- β -cyclodextrin

Eight gram of β -CD was dissolved in 70 mL of 96% KOH. The solution was agitated and heated in 50 °C water bath for 1 h, and then 7.5 g of glycine was added, simultaneously, 10 g of chloroepoxy propane was added dropwise into the above solution and reacted for 1 h at 60 °C, and then cooled to room temperature. pH was adjusted to about 5.5 with sulphuric acid, and 150 mL of

absolute ethylalcohol was added, and then filtered, evaporated and concentrated in water bath for removal of residual ethylalcohol. Then, 300 mL of methanol was added and kept overnight, filtered and dried to give white, solid glycine- β -cyclodextrin, the reaction scheme for the synthesis was shown in Fig. 1. GCD was confirmed by Nicolet FT-IR 5700 infrared spectrophotometer (Thermo, Madison, USA).

2.5. Solubilization experiments

For the solubility measurements of phenanthrene, 10 mL of solution containing varying concentrations of CD (0–12 g/L for β -CD, 0–30 g/L for GCD and 0–30 g/L for CMCD) were poured in 50 mL conical flasks with caps and the solid phenanthrene was added in quantities in excess of the solubility limit. The conical flasks were equilibrated on a reciprocating shaker for 24 h at 25 ± 1 °C, and then the mixture solution was centrifuged at 4000 rpm for 30 min. The solubility of phenanthrene was determined by measuring the solution absorbance at 254 nm after being diluted with 50:50 methanol/water. The role of methanol is to decompose the CD inclusion complexes, hereby keeping the UV spectrum unchanged [16].

For the solubility measurements of lead carbonate, 10 mL of solution containing varying concentrations of GCD, CMCD and β -CD were poured in 50 mL conical flasks with caps, and the solid lead carbonate was also added in quantities in excess of the solubility limit. The background ionic strength was controlled by 50 mM KNO_3 . Hydrogen ion activity was adjusted to $\text{pH } 6.00 \pm 0.05$ in all GCD, CMCD and β -CD solutions before adding the metal salts. The pH was not controlled during the experiment to avoid interference with buffering compounds, the final pH varied from 5.3 to 7.3. The conical flasks were equilibrated on a reciprocating shaker for 24 h at 25 ± 1 °C, and then the mixture solution was centrifuged at 4000 rpm for 30 min. The aqueous lead concentration was subsequently analyzed with AAS.

2.6. Batch desorption experiments

The desorption of lead and phenanthrene from contaminated soils with different solutions were measured in batch experiments. A weight of 0.5 g of contaminated soil samples was weighed into 50 mL conical flasks, to which 25 mL of GCD solutions with different concentrations were added. All aqueous solutions for soil test contained 50 mM KNO_3 to keep a constant ionic strength and 0.01% (w/w) NaN_3 to inhibit microbial growth. The pH of soil suspension was adjusted to 6.0 with 0.1 mol/L HNO_3 . The conical flasks were equilibrated on a reciprocating shaker for 24 h at 25 ± 1 °C, and then the mixture solution was centrifuged at 4000 rpm for 30 min. The phenanthrene concentration in the solution was determined by HPLC, and the aqueous lead concentration was analyzed with AAS.

3. Results and discussion

3.1. Characterization of GCD

The FT-IR spectra of glycine, β -CD and GCD are shown together in Fig. 2. Compared with the FT-IR spectra of β -CD, the FT-IR spectra of GCD is similar. Some characteristic absorption peaks of β -CD at 857, 946, 1028 and 1159 cm^{-1} have been also found in the FT-IR spectra of GCD [17], which indicates that cavity structure of β -CD was kept in GCD molecular. In addition, absorption peaks obviously shifted to higher wave number and ranged widely between 3500 and 3100 cm^{-1} . It is because that addition reaction happened between ring opening epoxy groups and amino groups,

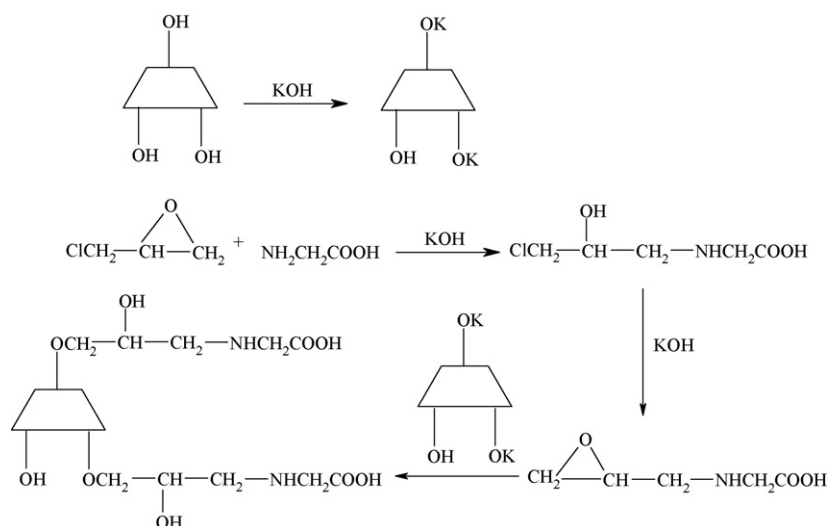


Fig. 1. Reaction scheme for the synthesis of GCD.

and a kind of new NH bond was obtained and exhibited overlapping absorption peaks with hydroxyl groups. The characteristic absorption peak of carboxyl group at 1408 cm^{-1} was also found in the IR spectra of GCD, which indicates that amino group and carboxyl group from glycine were grafted to molecular scaffold of $\beta\text{-CD}$.

3.2. Characterization of complexation of phenanthrene and lead by GCD

GCD can form host/guest inclusion complex with phenanthrene, the inclusion complex was characterized with fluorescence spectra, the results are shown in Fig. 3. Fig. 3 shows that the fluorescence intensity of phenanthrene decrease with increasing concentration of GCD. Coordination of lead with GCD was characterized with UV spectra, absorbance spectra for GCD, Pb^{2+} , and lead–GCD mixtures are presented in Fig. 4. For addition of GCD to Pb^{2+} solutions, the spectral shifts were more dramatic, absorbance below 270 nm was significantly increased, and a shoulder peak was also appeared at approximately 240 nm. These spectral changes indicate the formation of a GCD– Pb^{2+} complex. For GCD, nitrogen and oxygen in the amino group and carboxyl group are likely responsible for lead binding.

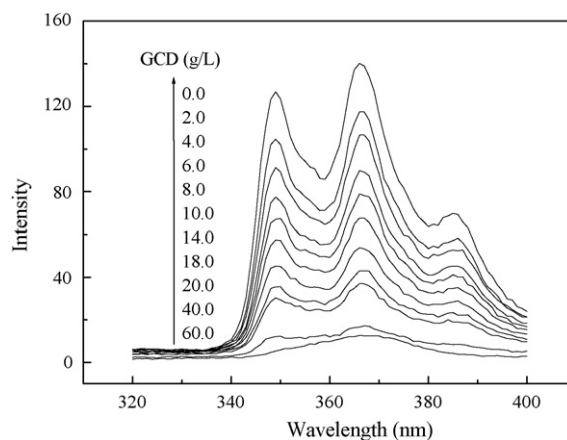


Fig. 3. The fluorescence spectra of phenanthrene/GCD inclusion complex; [phenanthrene] = 0.01 mg/L; $\lambda_{\text{ex}} = 249\text{ nm}$.

3.3. Solubilization of phenanthrene

The solubilization effects of $\beta\text{-CD}$, GCD and CMCD on phenanthrene are plotted in Fig. 5. The results show the apparent aqueous solubilities of phenanthrene are linearly increased with increasing $\beta\text{-CD}$, GCD and CMCD concentration. This phenomenon is

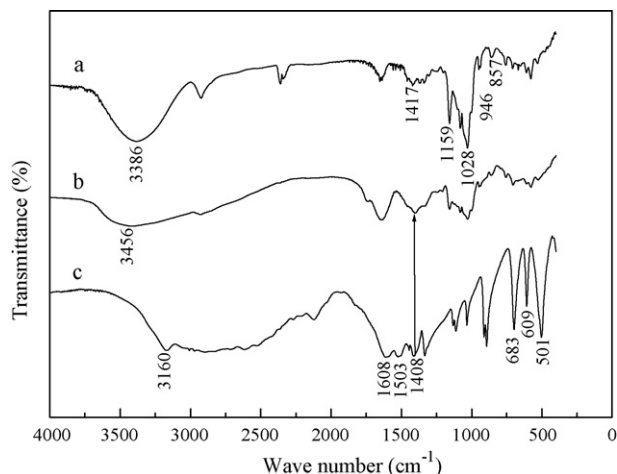


Fig. 2. FT-IR spectra of $\beta\text{-CD}$ (a), GCD (b) and Glycine (c).

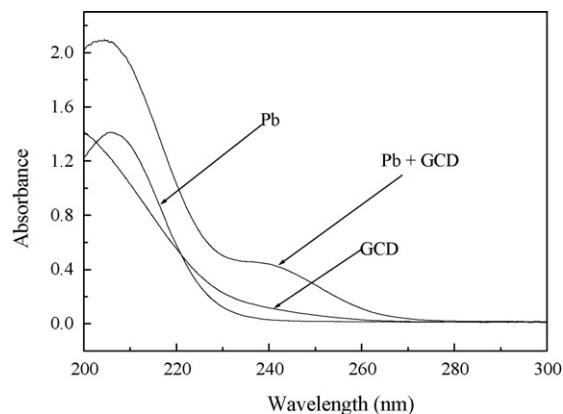


Fig. 4. Absorbance spectra of for GCD, Pb^{2+} , and lead–GCD mixtures; [GCD] = 0.5 g/L; [Pb $^{2+}$] = 0.01 g/L.

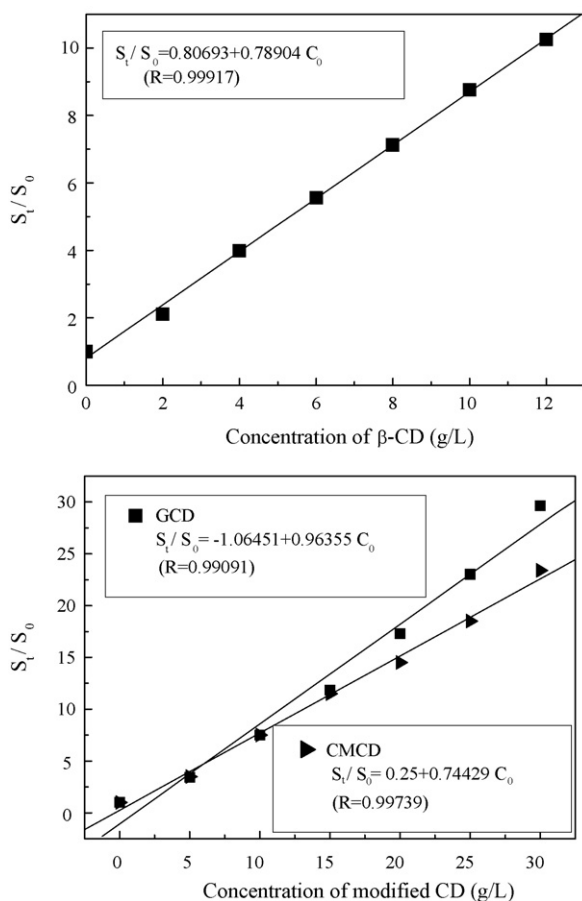


Fig. 5. Solubilization curves of phenanthrene in β -CD, GCD and CMCD; $T = 25^\circ\text{C}$; pH 6.0; time = 24 h.

attributed to the formation of 1:1 inclusion complexes [10]. The linear relationship can be expressed by as follows:

$$\frac{S_t}{S_0} = 1 + K_f C_0 \quad (1)$$

where S_t is aqueous-phase concentration of phenanthrene in the presence of CD, S_0 is concentration of phenanthrene in the absence of CD, C_0 represents the initial concentration of CD and K_f is the stability constant of inclusion complexes for phenanthrene with CD, and it was used to evaluate solubilization capacity of CD for phenanthrene. As shown in Fig. 5, the stability constant of inclusion complex for phenanthrene with β -CD, GCD and CMCD is 0.78904, 0.96355 and 0.74429, respectively, higher binding constant was found for phenanthrene with GCD than with β -CD (or CMCD), which indicates that solubilization capacity of GCD for phenanthrene is higher than that of β -CD (or CMCD) for phenanthrene. The GCD has obvious solubilization for phenanthrene, the solubility of phenanthrene in 30 g/L of GCD was enhanced about 30-fold.

3.4. Solubilization of lead carbonate

Because of coordination between lead and GCD, GCD can enhance the solubility of lead carbonate. The solubilization effects of GCD on lead carbonate are plotted in Fig. 6. The results show the apparent aqueous solubilities of lead carbonate are obviously increased with increasing GCD concentration, when the concentration of GCD reached 20 g/L, the aqueous lead concentration was 2945 mg/L, and the solubilization effects of GCD on lead carbonate are obviously higher than those of CMCD on lead carbonate. In addition, the aqueous solubilities of lead carbonate did not change

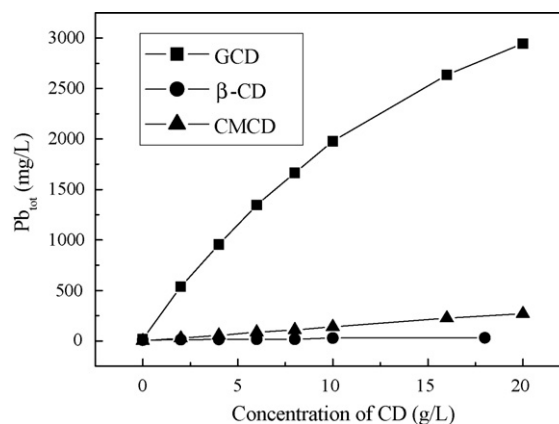


Fig. 6. Enhanced lead carbonate solubility as a function of GCD concentration; $[\text{KNO}_3] = 50 \text{ mM}$; $T = 25^\circ\text{C}$; pH 6.0; time = 24 h.

with the concentration of β -CD. It was because that β -CD does not complex metal ions but GCD (or CMCD) does.

3.5. Adsorption of GCD onto soils

During the desorption process, the adsorption of CDs onto soils is also an important parameter in affecting the removal efficiency of phenanthrene and lead from contaminated soils. Under the conditions of 0.5 g clean soils, pH 6.0, 25°C and initial CD concentration (2.0, 4.0, 8.0 and 10.0 g/L). The adsorption of β -CD and GCD onto soils was shown in Fig. 7. The results show that adsorption efficiencies of β -CD and GCD onto soil are both below 10%, and the adsorption efficiencies of GCD onto soil are lower than those of β -CD onto soil, it was because that the water-solubility of GCD is higher than that of β -CD. These data illustrate the higher potential capacity of GCD than β -CD to enhance phenanthrene and lead desorption from the contaminated soils.

3.6. Desorption kinetics of phenanthrene and lead

Under the conditions of 0.5 g contaminated soils, pH 6.0, 25°C and 50 mL of 10 g/L GCD, the desorption kinetics of phenanthrene and lead from contaminated soils was studied. The pseudo-first-order and pseudo-second-order models were used to test the experimental data [18,19].

The pseudo-first-order kinetic model is given as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

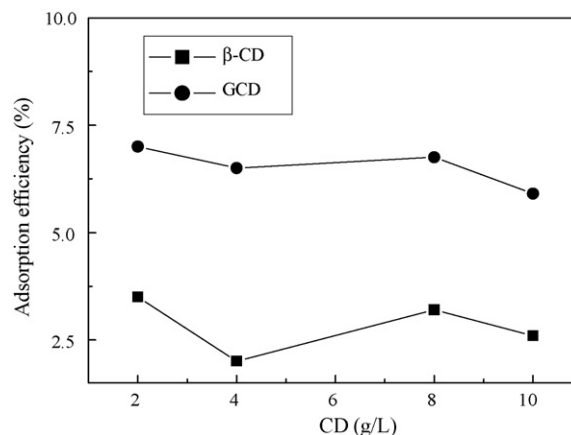


Fig. 7. The adsorption of β -CD and GCD onto soils; $T = 25^\circ\text{C}$; pH 6.0; time = 24 h.

Table 1
Desorption kinetic parameters of phenanthrene and lead from co-contaminated soil.

Kinetics model	Value	
	Phenanthrene	Lead
Pseudo-first-order		
k_1 (min^{-1})	0.03437	0.02696
$Q_{e,\text{cal}}$ (mg g^{-1})	0.04860	0.790
R^2	0.9573	0.9081
Pseudo-second-order		
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	1.393	0.06534
$Q_{e,\text{cal}}$ (mg g^{-1})	0.08756	1.259
R^2	0.9968	0.9938
$Q_{e,\text{exp}}$ (mg g^{-1})	0.08338	1.230

where Q_e is equilibrium desorption amount (mg/g), Q_t is desorption amount at time t (mg/g) and k_1 is the pseudo-first-order rate constant (min^{-1}). A straight line plot of $\ln(Q_e - Q_t)$ versus t will give the values of k_1 and Q_e from the slope and intercept, respectively. The rate constant and correlation coefficient for phenanthrene and lead desorption are shown in Table 1. The calculated value of desorption amount for phenanthrene and lead is 0.04860 and 0.790 mg g^{-1} , respectively, both of them are lower than the value of experimental desorption amount (0.08338 mg g^{-1} for phenanthrene, 1.230 mg g^{-1} for lead). The $Q_{e,\text{cal}}$ and $Q_{e,\text{exp}}$ values both for phenanthrene and lead were not in agreement with each other. Therefore, one can conclude that desorption of phenanthrene and lead did not follow pseudo-first-order model.

The pseudo-second-order kinetic model is given as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (3)$$

where k_2 is the rate constant of pseudo-second-order desorption ($\text{g mg}^{-1} \text{min}^{-1}$). A straight line plot of t/Q_t versus t will give the values of Q_e and k_2 from the slope and intercept, respectively. The rate constant and correlation coefficient for phenanthrene and lead desorption are also shown in Table 1. The calculated value of desorption amount for phenanthrene and lead is 0.08756 and 1.259 mg g^{-1} , respectively, both of them are close to the values of experimental desorption capacity (0.08338 mg g^{-1} for phenanthrene, 1.230 mg g^{-1} for lead). In addition, both for phenanthrene and lead, the correlation coefficient of the pseudo-second-order desorption equation is higher than that of the pseudo-first-order desorption equation. Therefore, it could be suggested that desorption of phenanthrene and lead from contaminated soil follows pseudo-second-order better than pseudo-first-order model, thus, the pseudo-second-order equation is suitable for desorption process of phenanthrene and lead from contaminated soil.

3.7. Simultaneous removal of phenanthrene and lead

The results from the FT-IR spectra of GCD show that CD cavity, amino groups and carboxyl groups were kept in the molecular structure of GCD. In order to investigate simultaneous complexation of phenanthrene and lead in aqueous systems by GCD, firstly, the same dosage of lead carbonate was added to aqueous solution with 10 g/L GCD and different concentration of phenanthrene. Solubilization experiments of lead carbonate were investigated in the presence of phenanthrene, the results show that the apparent aqueous solubilities of lead carbonate are almost not affected by concentration of phenanthrene, which indicates that the presence of phenanthrene has a negligible effect on the complexation Pb^{2+} by GCD (Fig. 8a). Secondly, the same dosage of phenanthrene was added to aqueous solution with 10 g/L GCD and different concentration of Pb^{2+} . Solubilization experiments of phenanthrene were also investigated in the presence of Pb^{2+} , the results show that the

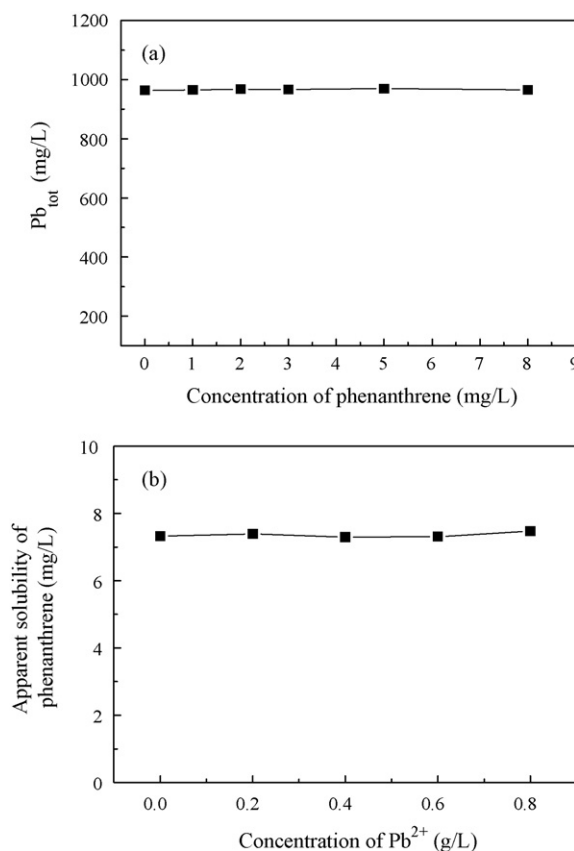


Fig. 8. Simultaneous complexation of phenanthrene and lead; [GCD]=10 g/L; $[\text{KNO}_3]=50 \text{ mM}$; $T=25^\circ\text{C}$; $\text{pH } 6.0$.

apparent aqueous solubilities of phenanthrene are also not affected by concentration of Pb^{2+} , which indicates that the solubilization of phenanthrene by GCD was also not influenced by the presence of Pb^{2+} (Fig. 8b). It was because that phenanthrene and Pb^{2+} are complexed at different locations. The amino group and carboxyl groups of GCD complex the Pb^{2+} outside the cavity, whereas the phenanthrene was complexed by inclusion in the cavity.

Based on the above studies, GCD has the potential for simultaneous removal of heavy metal and PAHs from co-contaminated soils. The removal of both phenanthrene and lead from the co-contaminated soils by GCD were presented in Fig. 9. The removal efficiencies of phenanthrene and lead increased dramatically with the increasing GCD concentrations. At concentration of 40 g/L, GCD has a removal efficiency of 85.8% and 78.8% for lead

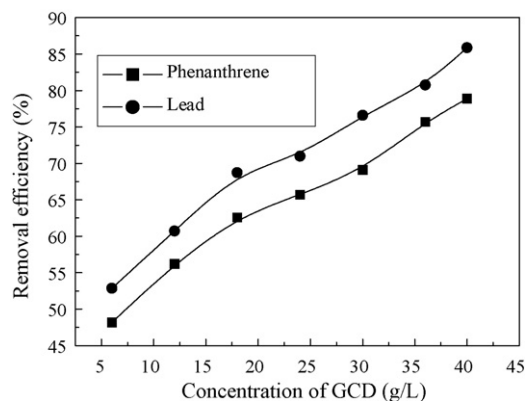


Fig. 9. Removal efficiency of phenanthrene and lead from co-contaminated soil; $T=25^\circ\text{C}$; $\text{pH } 6.0$; $\text{time}=24 \text{ h}$.

and phenanthrene, respectively, from the combined contaminated soil.

4. Conclusions

GCD could simultaneously increase the apparent aqueous solubility of phenanthrene and complex with lead. The solubility of phenanthrene in 30 g/L of GCD was enhanced about 30-fold, when the concentration of GCD reached 20 g/L, the aqueous lead concentration was 2945 mg/L. The desorption process of GCD for phenanthrene and lead from co-contaminated soil followed the pseudo-second-order kinetic model. The removal efficiencies of phenanthrene and lead increased dramatically with the increasing GCD concentrations. At concentration of 40 g/L, GCD has a removal efficiency of 85.8% and 78.8% for lead and phenanthrene, respectively, from the combined contaminated soil. GCD could be suitable for the removal of heavy metal and HOCs from co-contaminated soils.

Acknowledgements

This work was financed by the Natural Science Foundation of China (40861017, 50968001), the Natural Science Foundation of Jiangxi, China (2007GZH0477) and the Science Funds of the Education Office of Jiangxi, China (GJJ09261). The authors thank the anonymous reviewers for their comments.

References

- [1] M. Shin, S. Barrington, Effectiveness of the iodine ligand along with two surfactants on desorbing heavy metals from soils, *Water Air Soil Pollut.* 161 (2005) 193–208.
- [2] M. Shin, S.F. Barrington, W.D. Marshall, J.W. Kim, Effect of surfactant alkyl chain length on soil cadmium desorption using surfactant/ligand systems, *Chemosphere* 58 (2005) 735–742.
- [3] L. Lazzari, Correlation between inorganic (heavy metals) and organic (PCBs and PAHs) micropollutant concentrations during sewage sludge composting processes, *Chemosphere* 41 (2000) 427–435.
- [4] Q.T. Liu, M.L. Diamond, S.E. Gingrich, J.M. Ondov, P. Maciejczyk, G.A. Stern, Accumulation of metals, trace elements and semi-volatile organic compounds on exterior window surfaces in Baltimore, *Environ. Pollut.* 122 (2003) 51–61.
- [5] W.H. Zhang, D.C. Tsang, I.M. Lo, Removal of Pb and MDF from contaminated soils by EDTA-and SDS-enhanced washing, *Chemosphere* 66 (2007) 2025–2034.
- [6] J.Y. Wang, X.J. Huang, C.M. Kao, O. Stabnikova, Simultaneous removal of organic contaminants and heavy metals from kaolin using an upward electrokinetic soil remediation process, *J. Hazard. Mater.* 144 (2002) 292–299.
- [7] S.S. Song, L.Z. Zhu, W.J. Zhou, Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant, *Environ. Pollut.* 156 (2008) 1368–1370.
- [8] H. Zhang, Z. Dang, L.C. Zheng, X.Y. Yi, Remediation of soil co-contaminated with pyrene and cadmium by growing maize (*Zea mays* L.), *Int. J. Environ. Sci. Technol.* 6 (2009) 249–258.
- [9] X. Wang, M.L. Brusseau, Solubilization of some low-polarity organic compounds by hydroxypropyl- β -cyclodextrin, *Environ. Sci. Technol.* 27 (1993) 2821–2825.
- [10] S.O. Ko, M.A. Schlautman, E.R. Carraway, Partitioning of hydrophobic organic compounds to hydroxypropyl- β -cyclodextrin: experimental studies and model predictions for surfactant-enhanced remediation applications, *Environ. Sci. Technol.* 33 (1999) 2765–2770.
- [11] M.L. Brusseau, X. Wang, W.Z. Wang, Simultaneous elution of heavy metals and organic compounds from soil by cyclodextrin, *Environ. Sci. Technol.* 31 (1997) 1087–1092.
- [12] X. Wang, M.L. Brusseau, Simultaneous complexation of organic compounds and heavy metals by a modified cyclodextrin, *Environ. Sci. Technol.* 29 (1995) 2632–2635.
- [13] X. Wang, I. Yolcubal, W. Wang, J. Artiola, R. Maier, M.L. Brusseau, Enhanced removal of mercury from soil by cyclodextrin, ramnolipid, and calciumchloride, *Environ. Toxicol. Chem.* 23 (2004) 1888–1892.
- [14] E.M. Martin, Cyclodextrins and their uses: a review, *Process Biochem.* 39 (2004) 1033–1046.
- [15] S. Gould, R.C. Scott, 2-Hydroxypropyl- β -cyclodextrin (HP- β -CD): a toxicology review, *Food Chem. Toxicol.* 43 (2005) 1451–1459.
- [16] M.L. Brusseau, X. Wang, Q. Hu, Enhanced transport of low polarity organic compounds through soil by cyclodextrin, *Environ. Sci. Technol.* 28 (1994) 952–956.
- [17] D. Zhao, L. Zhao, C.S. Zhu, Z.B. Tian, X.Y. Shen, Synthesis and properties of water-insoluble β -cyclodextrin polymer crosslinked by citric acid with PEG-400 as modifier, *Carbohydr. Polym.* 78 (2009) 125–130.
- [18] A. Bhatnagar, A.K. Jain, A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water, *J. Colloid Interface Sci.* 28 (2005) 49–55.
- [19] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on crosslinked chitosan beads, *J. Hazard. Mater. B* 93 (2002) 233–248.