Paper sludge as a feasible soil amendment for the immobilization of Pb^{2+}

Xiaojia He, Lei Yao, Zhu Liang, Jinren Ni*

*The Key Laboratory of Water and Sediment Sciences, Ministry of Education, Department of Environmental Engineering,
Peking University, Beijing 100871, China. E-mail: hexiaojia@iee.pku.edu.cn*

Abstract

The possibility of amending Pb^{2+} contaminated soil (S) with paper sludge (P) was investigated through adsorption and desorption experiments. The adsorption process of Pb^{2+} in soil containing paper sludge (SP) could be well described by pseudo second-order kinetic model and the Langmuir isotherm model. After P addition, the equilibrium time decreased greatly (from 28 to 8 hr) and the Pb^{2+} maximum adsorbed amount (Q_{max}) increased by a factor of more than three to 102.04 mg/g. Q_{max} reached its maximum as S:P was 9:1 (*m/m*) after 10 days contact between S and P. Moreover, Pb^{2+} adsorbed amount increased with the rise of pH during the adsorption process. Desorption experiments indicated that Pb^{2+} adsorption in SP was irreversible. The metal ion fraction was analyzed with Energy Dispersive Spectrometer and Environmental Scan Electron Microscope. As a result, the addition of P to soil was found to induce a decrease in the mobile forms. The Pb^{2+} complexes formation in the presence of carbonates was the main adsorption mechanism. Overall, the paper sludge could be one of the promising soil amendments for the remediation of soil with Pb^{2+} contamination.

Key words: paper sludge; Pb^{2+}; adsorption

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Introduction

Heavy metal contaminated soil has become a global environmental concern due to serious threat to plant growth and human health (Singth et al., 2003). Lead is one of the important heavy metal resources, but at the same time is one of the heavy metal pollutants commonly found in the soils under sewage irrigation and soils around mining industry. The Pb^{2+} contaminated soil is commonly treated by engineering remediation, physical remediation, chemical remediation and phytoremediation (Raskin et al., 1997; Sun et al., 2005; Guo et al., 2006). Recently, an alternative has been proposed to immobilize Pb^{2+} by adding soil amendments (lime, phosphate salt and Ca-montmorillonite); these high-performance remediation methods have potential advantages, especially when applied to large areas of contaminated soil, such as mine spoil heaps (Vangronsveld et al., 1995; Auboiroux et al., 1996; Bolan et al., 2003; Basta and McGowan, 2004). However, these traditional soil amendments always have high cost considering their large dosage. Therefore, it is worthy to find new cost-effective amendments to treat Pb^{2+} contaminated soil.

Paper sludge produced by the paper industry during papermaking and wastewater treatment has been a serious threat to the environment. In China, the paper industry generated more than 12 million tons/year of paper sludge

according to the 2005 annual statistical report (SEPAC, 2006). Landfill and incineration are the most popular disposal methods (Li and Chen, 1999), which have obvious disadvantages in terms of high cost, excessive use of land, and secondary pollution. Recently, it was shown that $[C_6H_{10}O_5]_n$ and $CaCO_3$, as the main constituents of the paper sludge, could be used efficiently to amend soil properties and immobilize heavy mentals in soil, respectively (Singh, 1971; Beyer et al., 1997; Wang et al., 2001; Guo et al., 2006). These characteristics hint that paper sludge could be an excellent amendment for the Pb^{2+} contaminated soil and the potential toxicity of the paper sludge has been proved less significant in previous investigations (Beyer and Mueller, 1995; Bellamy et al., 1995). In addition, paper sludge as an industrial solid waste hardly has any cost when used as an amendment. For these reasons, there is a strong trend towards the reutilization of paper sludge to amend Pb^{2+} contaminated soil. To our knowledge, there is no extensive study in this field and little is known about the remediation mechanism.

In this study, the adsorption process of Pb^{2+} in soil with paper sludge addition was investigated to demonstrate the capacity of the sludge to absorb Pb^{2+}, which could suggest the feasibility of reusing paper sludge to amend Pb^{2+} contaminated soil. Particular consideration is given to kinetic and thermodynamic characteristics of the adsorption process. The soil (S)–paper sludge (P) contact time, ratio and solution pH were also studied to optimize the adsorption operation. Desorption experiment was conducted

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* Corresponding author. E-mail: nijinren@iee.pku.edu.cn

to estimate the stability of the amendment. The adsorption mechanism is explored through metal ion fraction tests and Environmental Scan Electron Microscope (ESEM) and Energy Dispersive Spectrometer (EDS) analysis. The study provides a basis for practical applications of Pb^{2+} contaminated soil remediation using paper sludge as an amendment.

1 Materials and methods

1.1 Materials

Paper sludge was provided by the Gold East Paper Co. Ltd., Jiangsu, China. Table 1 lists the chemical composition of the paper sludge (pH 8.21). The soil obtained from Heibei Province, China, was classified as alfisol group according to the Chinese Soil Taxonomy (Gong et al., 1995). The characteristics of soil were as follows: pH 7.33, total organic carbon (TOC) 2.38%. The Pb^{2+} solution was prepared by $PbCl_2$ (analytical grade). The pH value of the initial Pb^{2+} solution was adjusted by using HCl solutions to 3.89 ± 0.01, in order to prevent precipitation or hydrolysis products in the solutions before treatment with the paper sludge.

1.2 Preparation of soil and paper sludge mixture

Paper sludge was dried, crushed and added to the soil (whose impurities had been removed). The mixture was kept in a plastic bottle at $(25 \pm 2)°C$ and maintained at constant wet conditions for a pre-determined period of 0, 2, 4, 6, 9 and 10 days. The mixture ratios of soil to paper sludge by weight were 9:1, 9:4 and 9:8. The samples obtained were denoted as SP1, SP2 and SP3. After treatment, all samples were oven-dried (at 60°C), crushed and passed through a 2.0-mm sieve.

1.3 Adsorption tests

Kinetic experiments were performed with 500 mL shaking flasks containing 250 mL of 4000 mg/L Pb^{2+} solutions on DDHZ-300 rotary shaker (Jiangsu Taicang Laboratorial Equipment Factory, China) at 200 r/min and 25°C for 46 hr. The initial adsorbents (S, P and SP1) concentration (X_0) was kept constant at 40.0 g/L. After being shaken for a period of time (0.5, 1, 2, 4, 8, 12, 22, 28, 34 and 46 hr), the samples were centrifugally separated for 30 min at 4000 r/min and the supernates were filtered by 0.45-μm membranes. The residual Pb^{2+} concentration in filtrate was analyzed by a Vario 6.0 flame atomic adsorption spectroscope (AAS; Analytik jena AG, Germany). Meanwhile, the pH in filtrate was measured by 201 acidimeter (Hanna instruments Ltd., Italy). All the experiments were conducted in triplicates and the mean values were recorded. Since there were three adsorbents, ten times to be sampled and each treatment being in

triplicates, the total number of treatments was 90 ($3 \times 10 \times 3$).

In the isotherm experiments, 4 g of samples were mixed with 100 mL Pb^{2+} solution (80, 400, 800, 2000 and 4000 mg/L) at 200 r/min and 25°C for the equilibrium time. To obtain a comprehensive knowledge of Pb^{2+} adsorption process, adsorbents included S, P, SP1 (0, 2, 4, 6, 9 and 10 days), SP2 (10 days) and SP3 (10 days). The Pb^{2+} solution after adsorption was collected and measured using the method mentioned above, with each treatment being in triplicates. The total number of treatments in the experiment was 150 ($5 \times 10 \times 3$). The Pb^{2+} adsorbed amount (Q) can be calculated by Eq. (1):

$$Q = (C_0 - C) \times V/m \tag{1}$$

where, C_0 (mg/L) and C (mg/L) are the initial and final Pb^{2+} concentrations, respectively; V (L) is the solution volume in the flask, m (g) is the dry mass of the absorbent, including S, P, and SP.

1.4 Desorption tests

A consecutive dilution technique was adopted for desorption tests. After adsorption equilibrium was reached, the samples with solution were separated using a centrifuge for 10 min at 4000 r/min. Then, 50 mL of the liquid phase was decanted, of which Pb^{2+} concentration was determined using AAS. Meanwhile, another 50 mL of deionized water was added into the residual mixed phase and shaken until equilibrium was reached again. The foregoing steps were repeated four times to obtain the irreversible parameter of adsorption-desorption (H), which can be calculated by Eq. (2) (Yang and Zhang, 2007):

$$H = \frac{b_{des}}{b_{ads}} \tag{2}$$

where, b_{ads} is the adsorption constant and b_{des} is the desorption constant.

1.5 Metal ion fraction tests

Metal ion fraction tests were studied with 1.0 g samples (soil and soil treated with sludge) following the absorption experiments ($C_0 = 1000$ mg/L, $X_0 = 40.0$ g/L solution). The fraction tests were conducted according to the five-step sequential extraction procedure (Tessier et al., 1979) and some adjustments were made considering the fibre in the paper sludge (Table 2). The Pb^{2+} concentrations in solutions of five chemical species were determined by AAS.

1.6 EDS and ESEM analysis

The elemental compositions of SP before and after Pb^{2+} adsorption were determined by means of Quanta 200F EDS (FEI Company, USA). The surface morphologies

Table 1 Chemical composition of paper sludge

Industrial analysis (wt.%)			Organic element (wt.%)			Inorganic element (wt.%)		
Water	Volatile	Ash	C	H	N	Ca	Si	Al
40.60	56.31	45.68	25.36	2.63	0.13	16.2	0.49	0.40

Table 2   Chemical extraction scheme for metal fraction

Fraction	Extracting agents	Extraction conditions		
		Shaking time (hr)	Temperature (°C)	Separate method
Exchangeable	1 mol/L MgCl$_2$	1	25	Filtration
Carbonate bound	1 mol/L NaAc	5	25	Filtration
Fe/Mn bound	0.04 mol/L NH$_2$OH·HCl	5	96	Filtration
Organic-bound	68%HNO$_3$ + 30%H$_2$O$_2$	5	85	Centrifugation
	3.2 mol/L NH$_4$Ac	0.5	25	
Residual	68%HNO$_3$ + 40%HF + 38%HClO$_4$	2	160	Not needed

were examined with Quanta 200F ESEM (FEI Company, USA). Before analysis, the SP sample was washed three times with deionized water and dried until constant weight achieved.

2 Results and discussion

2.1 Adsorption kinetics

Figure 1 shows the adsorbed amounts (Q) of Pb^{2+} by S, P and SP1 against adsorption time. It is evident that Q for S increased gradually with time, but not at a particularly rapid rate and tailed off after about 28 hr. As a result, the equilibrium time required for Pb^{2+} adsorption onto S was taken to be 28 hr. Q for P increased rapidly with adsorption time over the first two hours, and saturated at about 4 hr; hence the equilibrium time for Pb^{2+} adsorption on P was taken to be 4 hr. The Q for SP1 behavior was similar to that of Q for P within the first two hours, and then the curve became smooth after 8 hr, indicating the equilibrium time for adsorption on SP1 was 8 hr. These results confirmed that the equilibrium time required for Pb^{2+} adsorption onto S decreased substantially (from 28 to 8 hr) due to paper sludge addition.

The kinetic models of dual constant and pseudo second-order were used to fit the adsorption data. The dual constant and pseudo second-order models are generally expressed as Eqs. (3) and (4), respectively (Ho, 1995; Yao et al., 2008):

$$Q_t = Kt^n \tag{3}$$

$$\frac{t}{Q_t} = \frac{1}{bQ_e^2} + \frac{t}{Q_e} \tag{4}$$

where, Q_t is the absorbed amount at any time t, K and n are rate constants in the dual constant equation, b is the rate constant of the pseudo second-order equation, Q_e is the theoretically absorbed amount at equilibrium.

It can be seen from Table 3 that although the adsorption rates conformed to both equations, better correlation was obtained using the pseudo second-order kinetic equation ($R^2 > 0.95$). Therefore, the results indicated that the kinetics of Pb^{2+} adsorption onto S, P, and SP followed pseudo second-order kinetic equation. In addition, previous research has established that bQ_e^2 value in the pseudo second-order kinetic equation is an important indicator of the adsorption rate; the higher bQ_e^2 value is, the faster the adsorption process will be (Luo, 2007). The differences between the bQ_e^2 values in Table 3 showed that bQ_e^2 value of Pb^{2+} adsorption on SP1 (0.6608) was greater than that of S (0.1164), indicating that the addition of paper sludge accelerated the process of Pb^{2+} adsorption onto S.
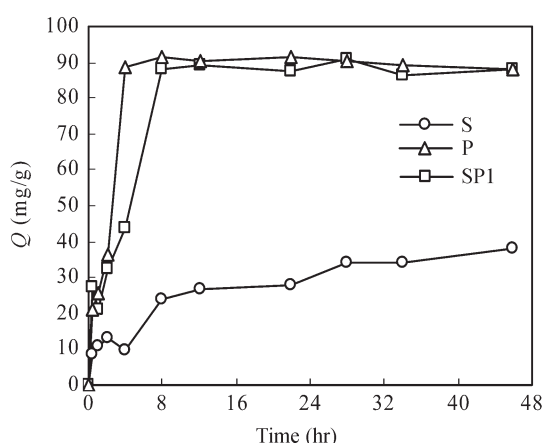
2.2 Adsorption isotherms

Based on the adsorption experiments, three isotherm models, i.e., linear, Freundlich and Langmuir, were selected to simulate the adsorption process. The linear isotherm is the idealist model which can be expressed by Eq. (5) (Yao et al., 2008):

$$Q_e = kC_e + a \tag{5}$$

where, C_e is the equilibrium concentration of Pb^{2+}, Q_e is the theoretically absorbed amount at equilibrium, k and a are constants of the Pb^{2+} absorption isotherm model.

The Freundlich isotherm carries out a monolayer sorption with heterogeneous energetic distribution of active sites, which can be expressed as Eq. (6) (Freundlich, 1906):

$$\log Q_e = \log K + \frac{1}{n}\log C_e \tag{6}$$

Fig. 1   Adsorption kinetic curves of Pb^{2+} onto S, P and SP1 absorbents.

Table 3   Adsorption kinetic equation fitting results

Adsorbent	Dual constant model			Pseudo second-order model		
	K	n	R^2	bQ_e^2	b	R^2
S	2.459	0.3444	0.8884	0.1164	7.042×10^{-5}	0.9569
P	8.061	0.3380	0.7912	1.195	1.394×10^{-4}	0.9950
SP1	7.155	0.3432	0.8580	0.6608	7.425×10^{-5}	0.9918

where, K and n are the indicators of absorption density and intensity.

The Langmuir isotherm proposes that uptake of matter occurs on a homogeneous surface. It can be presented as Eq. (7) (Langmuir, 1918):

$$\frac{1}{Q_e} = \frac{1}{bC_eQ_{max}} + \frac{1}{Q_{max}} \tag{7}$$

where, Q_{max} is the maximum adsorbed amount of Pb^{2+}, b is the constant related to the affinity of the binding sites.

Table 4 lists the parameters related to the three models. The correlation coefficients (R^2) of the linear isotherm model and Freundlich model were low (mostly less than 0.9), suggesting these two models did not fit the adsorption data appropriately. However, the adsorption processes related to S, P, and SP1 were properly represented by the Langmuir model, for which R^2 invariably exceeded 0.99. This agreement with the Langmuir model may indicate various physical and chemical functions occurred in the Pb^{2+} adsorption process. Moreover, the maximum adsorbed amount Q_{max} of S and P from Langmuir model were almost the same (28.90 and 28.98 mg/g) and Q_{max} of SP1 at day 10 was 102.04 mg/g, an increase of a factor of more than three. The results confirmed that the addition of paper sludge could increase the adsorption capability of soil to remediate Pb^{2+} pollution. This positive effect was possibly due to the presence of organic material such as fiber and tannin (Calace et al., 2003) and the presence of inorganic material such as $CaCO_3$ (Xia, 2000) in the paper sludge. From Table 4 it can also be seen that the peak Q_{max} (102.04 mg/g) for SP was approximately one and half times as much as the sum of Q_{max} for S and P (57.88 mg/g). This demonstrated that new adsorbed sites, formed during the contact process between P and S, contributed to increase the adsorption capability of the SP system. Microorganisms in soil can break down long fibers in paper sludge into particle organic matter, which has more adsorbed sites, such as hydroxyl functional groups (Balabane et al., 1999; Balabane and Oort, 2002; Gregorich et al., 1995). Moreover, the presence of carbonates in paper sludge can increase new amphoteric ligand adsorbed sites on the edges of clay minerals in soil (Bereket et al., 1997; Mercier and Detellier, 1995; Strawn and Sparks, 1999). All these new adsorbed sites formed during contact induced a larger adsorption capability of SP than that of S or P alone.
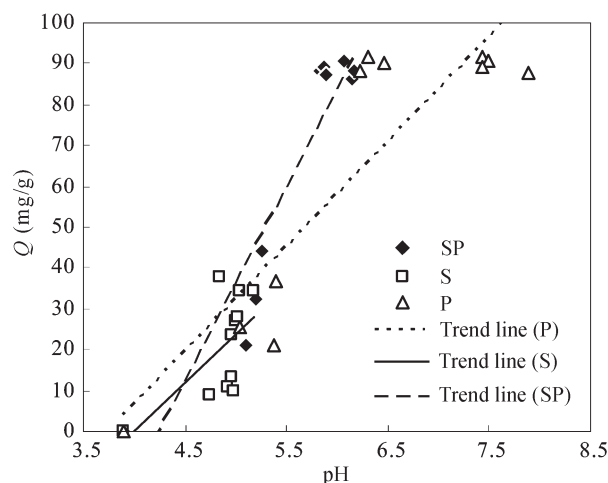

Fig. 2 Relationship between Q and pH.

Table 4 also shows that Q_{max} for SP1 increased slowly during the first 6 days, and then increased markedly until day 9, after which the Q_{max} achieved constant at day 10. Hence, 10 days was selected as the optimal contact time for further study in this article. The Q_{max} increased with the contact time between S and P could also be attributed to new adsorbed sites formation during the contact process mentioned above. Moreover, from SP1 to SP3 the Q_{max} at day 10 decreased with the increasing of paper sludge addition ratio. When the dosage of paper sludge was too large, there were not enough microorganisms or clay minerals in soil which can react with paper sludge to create new adsorbed sites. Thus, new adsorbed sites decreased with the increasing dosage of P and led to Q_{max} decrease of SP. Q_{max} was the maximal value when S:P reached 9:1 (*m/m*) after S and P contact for 10 days.

2.3 pH analysis

Figure 2 shows the relationship between Q and corresponding pH observed in kinetic experiments. As is shown, Q increased as pH increased for all of the systems (S, P and SP). This is because paper sludge addition could increase the pH of the SP system and Pb^{2+} complex may be formed as a result. Therefore, Pb^{2+} concentration in a higher pH solution became lower than the initial one which was presented as Q increase.

After statistical analysis of data in isotherm experiments, a single algorithm relating C_0, Ce and pH was

Table 4 Adsorption isotherm equation fitting results

Adsorbent-time	Linear isotherm			Freundlich isotherm			Langmuir isotherm		
	K	a	R^2	K	n	R^2	Q_{max} (mg/g)	b	R^2
S-10 day	8.139×10^{-3}	5.624	0.7260	1.410	2.817	0.7038	28.90	0.0083	0.9298
P-10 day	1.357×10^{-2}	7.965	0.5431	4.317	3.626	0.7331	28.98	0.1548	0.9927
SP1-0 day	3.267×10^{-2}	8.083	0.7442	5.126	3.218	0.7564	28.74	0.3327	0.9900
SP1-2 day	7.127×10^{-2}	7.046	0.8235	4.713	2.696	0.8490	35.84	0.1649	0.9987
SP1-4 day	4.026×10^{-2}	8.100	0.7746	5.537	3.204	0.7399	39.06	0.2476	0.9953
SP1-6 day	2.088×10^{-2}	8.097	0.6513	4.797	3.495	0.6556	45.87	0.1148	0.9949
SP1-9 day	5.146×10^{-2}	7.677	0.9492	4.527	2.772	0.8266	102.04	0.0370	0.9939
SP1-10 day	4.230×10^{-2}	8.110	0.9421	5.694	2.826	0.8152	102.04	0.0743	0.9988
SP2-10 day	2.559×10^{-2}	8.120	0.6969	5.418	3.555	0.6700	53.48	0.1460	0.9969
SP3-10 day	3.836×10^{-2}	8.112	0.7673	5.636	3.287	0.7153	46.51	0.1994	0.9962

carried out using Stata software, giving the following fit:

$$\ln C_0 - 0.4 \times \ln C_e = -0.6 \times pH^2 + 8 \times pH - 20 \qquad (8)$$

Equation (8) has R^2 value (ca., 0.900), and so appears to fit correctly the relationship between C_0 and C_e and pH. Statistical analysis showed that pH was a more significant factor than either C_0 or C_e. Equation (8) was nonlinear in pH, unlike that obtained by other studies (Jopony and Young, 1994), in which the relationship was linear. The difference was simply due to P addition amplifying the effect of pH on the SP system compared to that of S alone. With Eq. (8), concentrations of Pb²⁺ in solution ($-\ln C_e$) could be predicted, given $\ln C_0$ and pH. Figure 3 shows a comparison between the measured concentrations of Pb²⁺ in solution and those predicted from the equation. Clearly, there was a good agreement; the calculated model efficiency (Miehle et al., 2006) was 0.897. Thus, Eq. (8) performed well to predict concentrations of Pb²⁺ in solution.

2.4 Desorption results

Whether paper sludge addition was a potential pollution to surface and underground water when rainfall occurred? This should be verified. Therefore, a desorption test was conducted to investigate the stability of the adsorption behavior of Pb²⁺ onto soil with paper sludge addition (Table 5). It should be noted that b_{ads} and b_{des} were relative to the adsorption affinity and the desorption affinity, respectively. H reflected the degree of reversibility of the adsorption-desorption process, where $H = 1$ implies reversibility and the further H is from unity the more serious the hysteresis effect is.
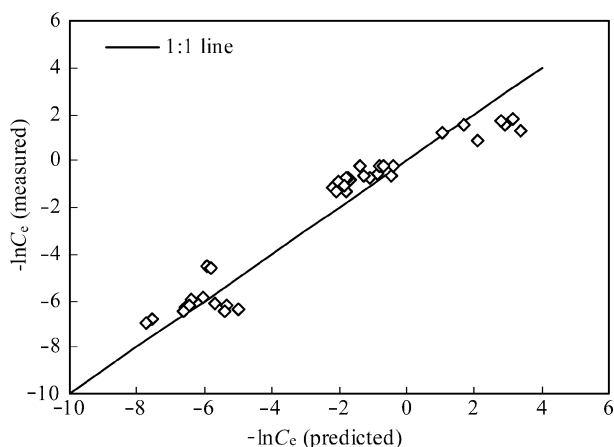
In the present study, $H(S) \approx 1$, indicating Pb²⁺

adsorption-desorption process was reversible, and therefore desorption for S was most straightforward. Whereas, the H values of P, SP1-10 day, SP2-10 day and SP3-10 day were $\ll 1$, demonstrating Pb²⁺ adsorption-desorption process was irreversible; the hysteresis effect was observed in these systems. One reason for this is that Pb²⁺ complexes (hard to be desorbed) formed in the presence of paper sludge in the presence of carbonate which will be proved by the analysis in Sections 2.5 and 2.6. Another reason is that the organic carbon in SP was increased by the addition of paper sludge which is rich in fibre. Pusion et al. (2003) have proposed that the greater the proportion of organic carbon presents, the more serious the hysteresis effect will be. Thereby, the addition of paper sludge enhanced the hysteresis effect as a result of introducing higher organic carbon. In short, the adsorption behavior of Pb²⁺ in soil with paper sludge addition was irreversible and there was no potential pollution to surface and underground water.

2.5 Metal ion fraction test

The fraction of five chemical species of Pb²⁺ extracted from original soil (S) and soil treated with paper sludge (PS) is presented in Fig. 4. Exchangeable portion (step A) was the highest fraction of 48.50% from S, while carbonate-bound portion (step B) was the highest fraction of 73.54% from SP. An obvious decrease of Pb²⁺ content in step A (from 48.50% to 4.26%) was observed after the paper sludge was added. Conversely, the content of Pb²⁺ in step B increased from 34.45% to 73.54%, which was correlative to the decrease mentioned above. It could be attributed to the abundant CaCO₃ (Echeverria et al., 1998) present in paper sludge, indicating that the presence of carbonates had great contribution in the overall Pb²⁺ absorption process, which will be further discussed in
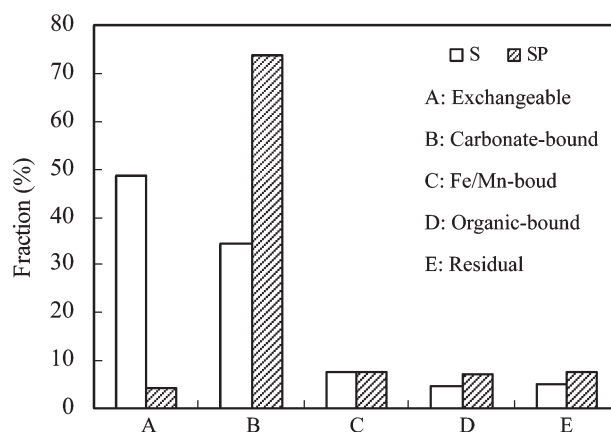

Fig. 3 Relationship between measured and predicted Pb²⁺ concentration in solution ($-\ln C_e$) (from Eq. (8)).

Fig. 4 Percentage of each species extracted from Pb²⁺-loaded S and SP ($C_0 = 1000$ mg/L, $X_0 = 40.0$ g/L).

Table 5 Irreversible parameters of adsorption/desorption

Adsorbent	Adsorption: Langmuir isotherm		Desorption: Langmuir isotherm		H
	b_{ads}	R^2	b_{des}	R^2	
S	0.0083	0.9298	0.0109	0.9775	1.3133
P	0.1548	0.9927	0.0022	0.9255	0.0142
SP1–10 day	0.0743	0.9988	0.0054	0.9800	0.0727
SP2–10 day	0.1460	0.9969	0.0140	0.9712	0.0959
SP3–10 day	0.1994	0.9962	0.0045	0.9905	0.0226

Section 2.6.

The addition of paper sludge induced a decrease of the total amount of mobile forms (step A + step B), particularly from 82.95% in soil to 77.80% in SP. This decrease corresponds to an increase in Pb^{2+} in step D (from 4.44% to 7.11%) and step E (from 5.00% to 7.51%), those portions of Pb^{2+} were found to be more stable forms. Moreover, the increase in step D was probably due to new metal bonds formed with organic matter, such as fibre and tannin (Calace et al., 2003), present in paper sludge. And the presence of aluminosilicate (Table 1) in the sludge could account for the increase of Pb^{2+} in the residue (step E).

2.6 EDS and ESEM analysis

The EDS and ESEM analysis were used to explore the mechanism of Pb^{2+} adsorption in soil with paper sludge addition. The results are shown in Table 6 and Fig. 5.

Table 6 shows that SP before and after adsorption mainly comprised three elements (C, O and Si). Moreover, Pb was not detected in SP before adsorption by EDS analysis. However, after adsorption the mass content (wt.%) of Pb reached 6.16%. Conversely, the mass contents of Na, Mg, Al, Si, K and Ca decreased by 34.3%, 22.6%, 34.3%, 20.0%, 66.0% and 35.2%, respectively. This could be due to the surface of SP being covered partly by Pb^{2+}

complexes. The ESEM analysis (Fig. 5) was therefore conducted to provide more detailed insight. In Fig. 5a, c, stripes, large particles and small particles were detected, respectively indicating fibre, soil and $CaCO_3$ in SP. In Fig. 5c, many smaller white particles can be seen located on the surface of the fibre and soil after Pb^{2+} adsorption, due to Pb^{2+} complexes formed as the result of strong affinity for Pb^{2+} by organic matter in fibre and clay mineral in soil (Strawn and Sparks, 1999). At higher magnification (8000 ×), Fig. 5b shows a single soil particle with a smooth surface. The small white particles mentioned above appear to be crystals, which partly cover the surface of

Table 6 Elemental compositions of SP before and after adsorption

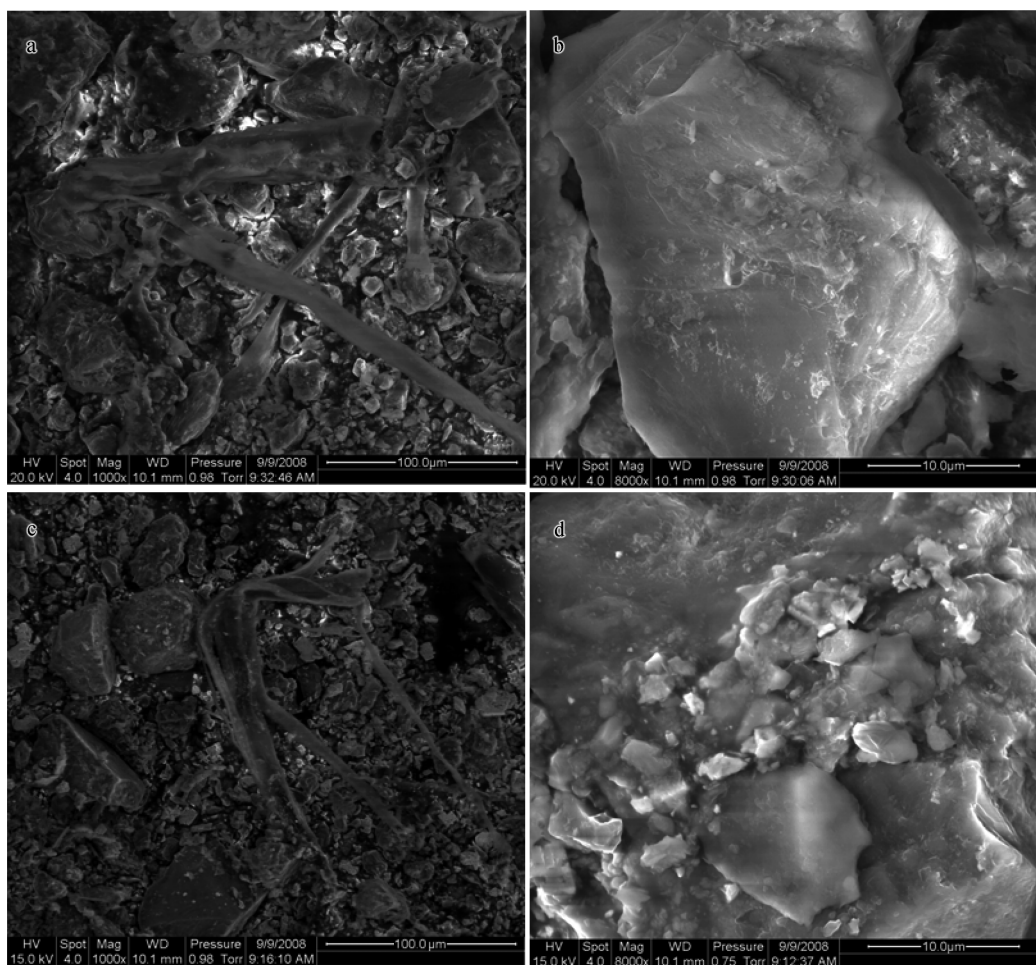| Element	Before adsorption		After adsorption	
	wt.%	at.%	wt.%	at.%
C	35.74	47.66	41.46	55.81
O	38.55	38.58	32.86	33.21
Na	1.02	0.71	0.67	0.47
Mg	1.37	0.90	1.06	0.70
Al	4.60	2.73	3.02	1.81
Si	12.10	6.90	9.68	5.57
K	1.97	0.80	0.67	0.28
Ca	3.32	1.33	2.15	0.87
Fe	1.33	0.38	1.39	0.40
Pb	0	0	6.16	0.48

wt.%: mass content; at.%: atomic content.

Fig. 5 ESEM photomicrographs of SP before and after adsorption. (a) before Pb^{2+} adsorption, 1000×; (b) before Pb^{2+} adsorption, 8000×; (c) after Pb^{2+} adsorption, 1000×; (d) after Pb^{2+} adsorption, 8000×.

the soil particle in Fig. 5d. The crystals could be PbCO$_3$ and Pb$_3$(OH)$_2$(CO$_3$)$_2$ formed by Pb^{2+} in the presence of carbonates, which could be mostly adsorbed by the fibre and soil particles in SP (Echeverria et al., 1998). This also can be supported by metal ion fraction test, in which carbonate-bound Pb^{2+} increased markedly after the addition of paper sludge.

3 Conclusions

We investigated the adsorption behavior of Pb^{2+} in soil for remediation with paper sludge addition. The adsorption process of Pb^{2+} in SP was well described by the pseudo second-order kinetic and the Langmuir isotherm models. After paper sludge addition, the equilibrium time required for Pb^{2+} adsorption decreased greatly. Furthermore, Q_{max} estimated from the Langmuir model increased by a factor of more than three, while Q increased with increasing pH. A single algorithm was developed to predict Pb^{2+} concentration in solution for given lnC_0 and pH. Using the Langmuir model, we showed that the Pb^{2+} adsorption-desorption process was irreversible. Further analysis by metal ion fraction tests demonstrated that the addition of paper sludge onto soil induced a decrease in mobile forms. Moreover, EDS and ESEM analysis revealed that adsorption was dominated by Pb^{2+} complexes formed in the presence of carbonates. Considering the effectiveness of paper sludge in immobilizing Pb^{2+}, the absence of harmful side effects, and its role as a fertilizer, this solid waste has a potential for remediation of soil contaminated with Pb^{2+}.

References

Auboiroux M, Baillif P, Touray J C, 1996. Fixation of Zn^{2+} and Pb^{2+} by a Ca-montmorillonite in brines and dilute solutions: Preliminary results. *Applied Clay Science*, 11: 117–126.

Balabane M, Faivre D, Oort F van, Dahmani-Muller H, 1999. Mutual effects of soil organic matter dynamics and heavy metals fate in a metallophyte grassland. *Environmental Pollution*, 105: 45–54.

Balabane M, Oort F van, 2002. Metal enrichment of particulate organic matter in arable soils with low metal contamination. *Soil Biology and Biochemistry*, 34: 1513–1516.

Basta N T, McGowen S L, 2004. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. *Environmental Pollution*, 127: 73–82.

Bellamy K L, Chong C, Cline R A J, 1995. Paper sludge utilization in agriculture and container nursery culture. *Journal of Environment Quality*, 2416: 1074–1082.

Bereket G, Aroguz A Z, Ozel M Z, 1997. Removal of Pb(II), Cu(II), Cd(II) and Zn(II) from aqueous solutions by adsorption on bentonite. *Journal of Colloid and Interface Science*, 187: 338–343.

Beyer L, Mueller K, 1995. Combined application of secondary paper mill sludges and cattle slurry: Soil risk or soil improvement. *Toxicological and Environmental Chemistry*, 47: 243–249.

Beyer L, Friind R, Mueller K, 1997. Short-term effects of a secondary paper mill sludge application on soil properties in a Psammentic Haplumbrept under cultivation. *Science of the Total Environment*, 197: 127–137.

Bolan N S, Adriano D C, Mani P, Duraisamy A, Arulmozhiselvan S, 2003. Immobilization and phytoavailability of cadmium in variable charge soils. II. Effect of lime compost. *Plant and Soil*, 251: 187–198.

Calace N, Nardi E, Petronio B M, Pietroletti M, Tosti G, 2003. Metal ion removal from water by sorption on paper mill sludge. *Chemosphere*, 51: 797–803.

Echeverria J C, Morera M T, Mazkiarin C, Garrido J J, 1998. Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environmental Pollution*, 101: 275–284.

Freundlich H M F, 1906. Over the adsorption in solution. *Journal of Physical Chemistry*, 57: 385–470.

Gregorich E G, Ellert B H, Monreal C M, 1995. Turnover and storage of corn residue carbon in a Gleysolic soil in eastern Canada. *Canadian Journal of Soil Science*, 75: 161–167.

Gong Z T, Lei W J, Gao Y X, Cao S G, Chen Z C, 1995. Chinese Soil Taxonomy (Revised version). China Agricultural Science and Technology Press, Beijing.

Guo G L, Zhuo Q X, Ma L Q, 2006. Availability and assessment of fixing additives for the *in situ* remediation of heavy metal contaminated soils: A review. *Environmental Monitoring and Assessment*, 116: 513–528.

Ho Y S, 1995. Absorption of heavy metals from waste streams by peat. Ph.D Thesis. University of Birmingham.

Jopony M, Young S D, 1994. The solid-solution equilibria of lead and cadmium in polluted soils. *European Journal of Soil Science*, 45: 59–70.

Langmuir I, 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40: 1361–1403.

Li Y M, Chen Z H, 1999. Research projects about utilization of pulp and paper industrial sludges. *Guangdong Papermaking*, 3: 22–24.

Luo X M, 2007. Case study on the migration and transform of arsenic in aquatic environment caused by gold mining. Ph.D. Thesis of China University of Geosciences. 52–64.

Mercier L, Detellier C, 1995. Preparation characterization and applications as heavy metals sorbents of covalently grafted thiol functionalities on the inter-lamellar surface of montmorillonite. *Environmental Science and Technology*, 29: 1318–1323.

Miehle P, Livesley S J, Feikemab P M, Lic C, Arndt S K, 2006. Assessing productivity and carbon sequestration capacity of *Eucalyptus globulus* plantations using the process model Forest-DNDC: Calibration and validation. *Ecological Modelling*, 192: 83–94.

Pusion A, Fiori M G, Braschi I, Gessa C, 2003. Adsorption and desorption of triasulfuron by soil. *Journal of Agricultural and Food Chemistry*, 51: 5350–5354.

Raskin L, Smith R D, Salt D E, 1997. Phytoremediation of metals: using plants to remove pollutants from the environment. *Current Opinion in Biotechnology*, 8: 221–226.

Singh M, 1971. Retention of added copper by two soils as affected by organic matter, CaCO₃, and exchangeable ions. *Geoderma*, 5: 219–227.

Singh O V, Labana S, Dey G, Hiraja R, Jain R K, 2003. Phytoremediation: An overview of metallic ion decontamination from soil. *Applied Microbiology and Biotechnology*, 61: 405–412.

SEPAC (State environmental protection administration of China), 2006. Annual Statistic 2005 Report on Environment in China. China Environmental Science Press, Beijing.

Strawn D G, Sparks D L, 1999. The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. *Journal of Colloid and Interface Science*, 216: 257–269.

Sun T H, Li P J, Zhou Q X, 2005. Formation Mechanism and Remediation Techniques for Contaminated Soil. Science and Technology Press, Beijing.

Tessier A, Campbell P G C, Bisson M, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51: 844–851.

Vangronsveld J, Colpaert J, Van Tichelen K, 1995. Reclamation of a bare industrial area contaminated by non-ferrous metals: Physico-chemical and biological evaluation of the durability of soil treatment and revegetation. *Environmental Pollution*, 94: 131–140.

Wang H, Zhou W, Lin B, 2001. Effect of calcium carbonate on adsorption and desorption of cadmium in soils. *Acta Ecologica Sinica*, 21: 932–937.

Xia H L, 2000. The application and development of CaCO₃ in paper industry. *Paper Chemicals*, 2: 5–8.

Yang Y T, Zhang Y P, 2007. Irreversible characteristic of lead(II) adsorption-desorption on soil clays. *Journal Northwest A & F University (Natural Science Edition)*, 35: 127–132.

Yao L, Ye Z F, Wang Z Y, Ni J R, 2008. Characteristics of Pb^{2+} biosorption with aerobic granular biomass. *Chinese Science Bulletin*, 53: 948–953.