



Humic substances as a washing agent for Cd-contaminated soils



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HIGHLIGHTS

- Leonardite is an excellent source of humic substances.
- Humic substances as a washing agent effectively removed Cd from contaminated soils.
- Cd in effluent was easily removed by Ca(OH)₂.

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ABSTRACT

Cost-effective and eco-friendly washing agents are in demand for Cd contaminated soils. Here, we used leonardite-derived humic substances to wash different types of Cd-contaminated soils, namely, a silty loam (Soil 1), a silty clay loam (Soil 2), and a sandy loam (Soil 3). Washing conditions were investigated for their effects on Cd removal efficiency. Cadmium removal was enhanced by a high humic substance concentration, long washing time, near neutral pH, and large solution/soil ratio. Based on the tradeoff between efficiency and cost, an optimum working condition was established as follows: humic substance concentration (3150 mg C/L), solution pH (6.0), washing time (2 h) and a washing solution/soil ratio (5). A single washing removed 0.55 mg Cd/kg from Soil 1 (1.33 mg Cd/kg), 2.32 mg Cd/kg from Soil 2 (6.57 mg Cd/kg), and 1.97 mg Cd/kg from Soil 3 (2.63 mg Cd/kg). Cd in effluents was effectively treated by adding a small dose of calcium hydroxide, reducing its concentration below the discharge limit of 0.1 mg/L in China. Being cost-effective and safe, humic substances have a great potential to replace common washing agents for the remediation of Cd-contaminated soils. Besides being environmentally benign, humic substances can improve soil physical, chemical, and biological properties.

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1. Introduction

Soil contamination by Cd is a common problem in many parts of the world, posing a threat to human health. In China, for example, Cd is the most commonly occurring metal contaminant in soils (The Ministry of Environmental Protection and the Ministry of Land and

Resources of the People's Republic of China, 2014). As Cd cannot be chemically or biologically degraded, immobilization or mobilization becomes the technology of choice for the remediation of soils that are contaminated with heavy metals (Bolan et al., 2014).

Immobilization may involve the addition to soil of solid adsorbents such as biochar (Yang et al., 2016; Lu et al., 2017; Wu et al., 2017), while mobilization is often achieved by washing soil with one or more of the following chemicals: metal chelating agents (e.g., EDTA), salts (e.g., CaCl₂, FeCl₃), strong acids (e.g., HCl, CH₃COOH), or surfactants (e.g., 1-dodecylpyridinium chloride) (Mulligan et al., 2001; Conte et al., 2005; Zeng et al., 2005; Makino et al., 2007, 2008, 2016; Kulikowska et al., 2015a,b; Guo et al., 2016).

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Based on a desorption process, soil washing is one of the most effective remediation techniques as it removes heavy metals from contaminated soils (Dermont et al., 2008). Soil washing, however, has the potential of causing problems. For example, the washing agent EDTA is difficult to decompose (Tandy et al., 2004; Zeng et al., 2005), and hence is detrimental to soil microbial health (Bucheli-Witschel and Egli, 2001), soil porosity (Heil et al., 1999), and groundwater quality. FeCl₃ and strong acids could acidify soil and adversely affect soil fertility and microbial activity (Rousk et al., 2009). Many washing surfactants are toxic to microbes, and their effluents could contaminate water bodies. Thus, there is an on-going search for cost-effective and eco-friendly washing chemicals. In this regard, humic substances have the potential of becoming the washing chemicals of choice (Soleimani et al., 2010; Kulikowska et al., 2015b). Besides being environmentally benign, humic substances can improve soil physical, chemical, and biological properties.

Humic substances are operationally divided into three fractions based on their solubility in alkali or acid, namely, humic acid which is, alkali-soluble, fulvic acid which is alkali- and acid-soluble, and humin which is insoluble in both alkali and acid. Humic substances have traditionally been viewed as a mixture of high molecular weight (>10,000 Da), randomly coiled, negatively charged macromolecules. This concept, however, is being displaced by one in which humic substances consist of aggregates of biologically derived molecules of relatively low molecular weight (200–3000 Da) bound by weak dispersive forces and forming micelles in solution (Theng and Yuan, 2008; Theng, 2012). Organic matter in soil is now broadly viewed as a continuum spanning the full range from intact plant material to highly oxidized carbon in carboxylic acids (Lehmann and Kleber, 2015).

Of particular relevance to the present investigation is the abundant occurrence in humic substances of carboxyl and phenolic hydroxyl groups, resulting in a cation exchange capacity (CEC) of 600–890 cmol(+)/kg for humic acid and 1000–1230 for fulvic acid (Tan, 2014) which is about 5–100 times higher than that of common clay minerals (Yuan et al., 2013). Humic substances can bind heavy metals by forming surface complexes with carboxyl and phenolic hydroxyl groups (Conte et al., 2005). Humic substances can be extracted from a variety of materials, such as leonardite and sewage sludge (Kulikowska et al., 2015a). Since leonardite may be likened as ancient biochar, the humic substances extracted from this source may be likened to a surface-activated biochar (Meng et al., 2016).

We have developed a humic substances-based technology to remove Cd from contaminated soils, involving the following steps: (1), extracting humic substances from leonardite; (2), using the humic substances as a washing agent; and (3), treating the resultant effluent (wastewater). To this end, we obtained water-soluble humic substances by treating leonardite with KOH, conducted batch experiments to determine the effects of humic substance concentration, liquid-solid ratio, solution pH, and washing time, on Cd removal efficiency, and then used calcium hydroxide to treat the washing effluent.

2. Materials and methods

2.1. Soil sampling and analysis

Samples of surface soil (0–30 cm) were collected from different regions in China (Table 1). Soil 1 and Soil 2 were taken from two contaminated farmlands near a nonferrous metal smelter in Hunan Province that has been in operation for many decades. Soil 3 was taken from an apple orchard in Yantai, Shandong Province, spiked with Cd(NO₃)₂ solution (12 mg Cd/L) at a solid:liquid ratio of 5 (g/

Table 1
Basic properties of soil samples.

	Unit	Soil 1	Soil 2	Soil 3
Sand content	%	40.5	24.8	81.9
Silt content	%	50.1	56.3	15.2
Clay content	%	9.4	18.9	2.9
Texture	–	Silty loam	Silty clay loam	Sandy loam
Organic carbon	%	2.16	1.88	1.73
pH (H ₂ O)	–	6.57	6.16	5.51
Total Cd	mg/kg	1.33	6.57	2.63

ml), and aged at room temperature for two months. After air-drying, grinding to pass a 2-mm sieve, and thorough mixing, the soil samples were analyzed for the following properties: (1), particle size using a Mastersizer 2000 (Marlvern, UK); (2), organic carbon using an elemental analyzer (Vario macro cube, Elementar, Germany); (3), pH in distilled water (1:5 w/v ratio) using a pH meter (Mettler Toledo, Switzerland); and (4), pseudo-total Cd concentration by placing 1 g of soil (dried at 105 °C) into a polytetrafluoroethylene vessel, adding a HCl:HNO₃ mixture (Sinopharm, China) at 3:1 ratio (v/v), and heating in a microwave oven (one-stage program; t = 160 °C). After cooling, the extracts were filtered through 0.45 μm membrane into 50 mL glass flasks, filled to the mark with ultra-pure water, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan DRC II, PerkinElmer, USA).

2.2. Humic substances and their analysis

The humic substances were obtained by extracting a leonardite from Shanxi Province with 0.1 M KOH, acidifying the extract to pH 7 with HCl, and keeping the supernatant. By operational definition, the derived humic substances comprise a mixture of water-soluble humic acid and fulvic acid. The high solubility of the material is of fundamental importance for our purposes as conventional humic acid is practically insoluble in water, and hence is unsuitable for use as a washing agent, while the cost of producing conventional fulvic acid is uneconomical for this purpose.

The humic substances were analyzed for (1), elemental composition using the same elemental analyzer mentioned above; (2), content of carboxyl and phenolic groups by an International Humic Substances Society method (IHSS, 2016); (3), surface tension at pH 6 using a tensiometer (Fangrui, China); (4), critical micelle concentration (CMC) by plotting surface tension against humic substance concentration; and (5), total heavy metal concentration by weighing 0.1 g of dried (105 °C) humic substances into a polytetrafluoroethylene vessel, adding a HClO₄:HNO₃:HF mixture (Sinopharm, China) at a 3:1:1 ratio (v/v/v), and heating in a microwave oven. The extracts were then filtered through 0.45 μm membrane into 50-mL glass flasks, filled to the mark with ultra-pure water, and analyzed with the same ICP-MS mentioned above.

2.3. Establishing optimum washing conditions

The washing efficiency of the humic substances from leonardite was compared with that of a commercial fulvic acid (Shanghai Macklin Biochemical Co., Ltd.) with a chemical formula of C₁₄H₁₂O₈, a molecular weight of 308.2 Da, a carboxyl content of 3.17 mol(+)/kg C, and a hydroxyl content of 3.04 mol(+)/kg C.

The effect of washing conditions on Cd removal efficiency was assessed by batch experiments conducted in duplicate at room temperature. Polyethylene tubes containing soil samples and solutions of either humic substances or fulvic acid were placed on a shaker, oscillating at 120 rpm. The variables included humic

substances or fulvic acid concentration (0, 157.5, 315, 630, 945, 1260, 1575, 1890, 2520, 3150, 3780, and 4725 mg C/L), solution/soil ratio (3, 5, 7, 9, 10, 12, 15, 20, 30 v/w), solution pH (3, 4, 5, 6, 7, 8, 9), and washing time (0.5, 1, 2, 4, 6, 8, 12 h). At the end of the washing cycle, the tubes were centrifuged at 3000 rpm for 15 min, the supernatants were filtered through a 0.45 μm membrane, and the concentration of the various metals was determined by atomic absorption spectrometry (AAS, TAS-990, China). Organic carbon was measured using a TOC-VCPH Total Organic Carbon Analyzer (Shimadzu, Japan).

2.4. Effluent treatment

An effluent sample was collected from washing experiment for treatment to remove Cd. A batch experiment (in duplicate at room temperature) was conducted to determine the effectiveness of calcium hydroxide for treating washing effluents. Briefly, 10 mL of effluent with a pH of 7.13 and a Cd concentration of 0.32 mg/L was placed in 15 mL polyethylene tubes, and 0.05, 0.1, 0.2, 0.3, 0.4 g $\text{Ca}(\text{OH})_2$ was added. After shaking at 120 rpm for 2 h on an oscillating shaker, the tubes were centrifuged at 3000 rpm for 15 min. The supernatants were filtered through a 0.45 μm membrane, and the concentration of Cd in the filtrate was determined by AAS (TAS-990, China).

2.5. Calculation and statistical analysis

Cd adsorption by humic substances was estimated from the difference in Cd concentration before and after washing the soil with the washing agent. Software OriginPro 8.0 (OriginLab, USA) was used for data analysis.

3. Result and discussion

3.1. Critical micelle concentration and total acidity of humic substances and fulvic acid

Critical micelle concentration (CMC) of a surfactant is the threshold concentration at which micelles begin to form. Its magnitude has a determining influence on the suitability of a given surfactant for use as a washing agent in that the smaller the CMC the better the washing efficiency (Mulligan et al., 2001; Mao et al., 2015). Fig. 1 shows that CMC of the leonardite-derived humic substances (1890 mg C/L at the corresponding surface tension of 54.6 mN/m) is lower than that of fulvic acid (3150 mg C/L at 47.62 mN/m). The humic substances would therefore be a better washing agent than the fulvic acid from Macklin. By comparison,

Kulikowska et al. (2015b) reported a CMC of 1101 mg C/L at pH 7 for humic substances from compost, increasing to 1215 mg C/L at pH 13.

In having a high concentration of carboxyl groups (6.70 mol(+)/kg C) and phenolic hydroxyl groups (5.44 mol(+)/kg C), the humic substances from leonardite would have a large propensity for adsorption of Cd and other metals by forming stable inner-sphere complexes with such groups (Tan, 2014). In order to desorb Cd from clay surfaces, the affinity of a washing agent for the metal contaminant should exceed that of soil clays.

3.2. Humic substances or fulvic acid concentration and Cd removal efficiency

As expected, the Cd removal efficiency of humic substances and fulvic acid increased with the concentration of the washing agent (Fig. 2). By forming complexes with humic substances (Yuan and Theng, 2011), soil clays would reduce the efficiency of washing agents in removing Cd from soil. For this reason, concentration higher than the CMC would be required for good washing effect. Furthermore, the higher the humic substance concentration, the more carboxyl and phenolic hydroxyl groups would be available for Cd complexation. For the same carbon concentration, humic substances could therefore remove more Cd from the contaminated soils as compared with fulvic acid.

Cd removal efficiency was markedly enhanced as the concentration of washing agent increased (0–4725 mg C/L). This effect was evident with humic substances than fulvic acid, particularly when the concentration of the washing agent was below the CMC. The Cd removal efficiency is much higher for Soil 3 than for either Soil 1 or Soil 2, probably because Soil 3 was lighter in texture (contained less clay), and had a shorter aging time of spiked Cd. We used a humic substance concentration of 3150 mg C/L (higher than its CMC) and adjust the liquid–solid ratio, pH, and washing time to optimize Cd removal efficiency.

3.3. Effect of liquid–solid ratio on Cd removal efficiency

As expected, Cd removal efficiency increased with liquid–solid ratio until a plateau was approached (Fig. 3). At a liquid–solid ratio of 20, Cd removal efficiency was 87.2% for Soil 1, and the residual Cd concentration was below the limit (0.30 mg/kg) set by the Ministry of Environmental Protection of People's Republic of China (2006). For Soil 3, a liquid–solid ratio of 15 was sufficient to reduce the Cd concentration to below the 0.30 mg/kg limit. For Soil 2, Cd removal efficiency increased rapidly to 80.2% as the liquid–solid rose from 3 to 20, and then rose slowly to 88.0% at a ratio of

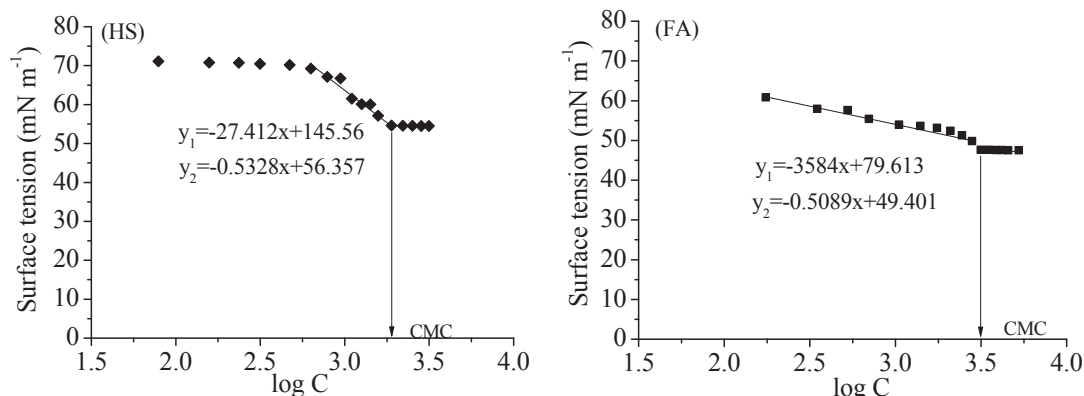


Fig. 1. Determination of the critical micelle concentration (CMC) by plotting surface tension against washing agent concentration (C).

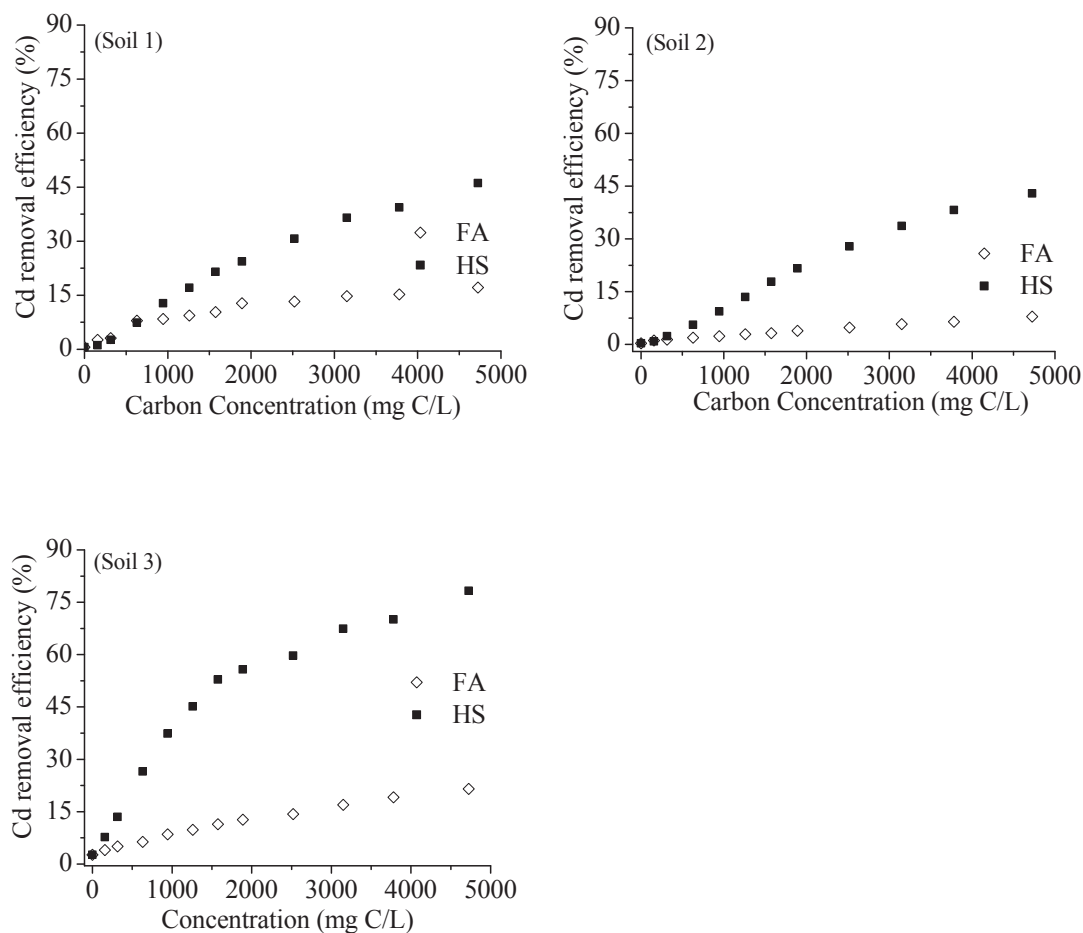


Fig. 2. The effect of washing agent concentrations on Cd removal efficiency. Experimental conditions: solution pH = 6.0, liquid-solid ratio of 5, washing time 12 h.

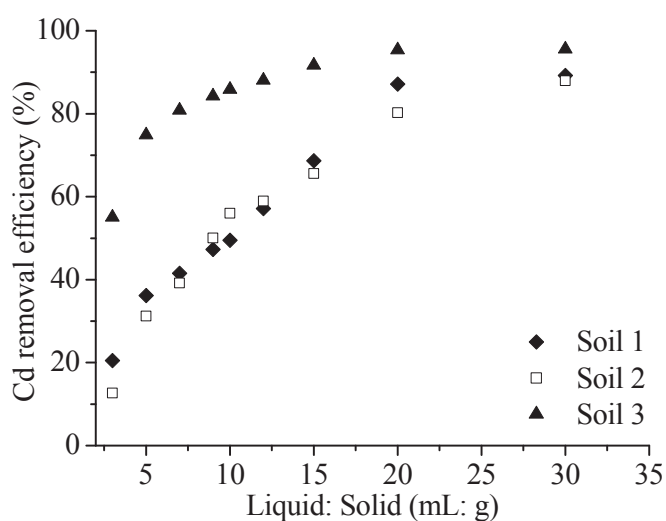


Fig. 3. The effect of liquid: solid ratio on Cd removal efficiency. Experimental conditions: solution pH: 6.0, washing time: 12 h, humic substance concentration: 3150 mg C/L.

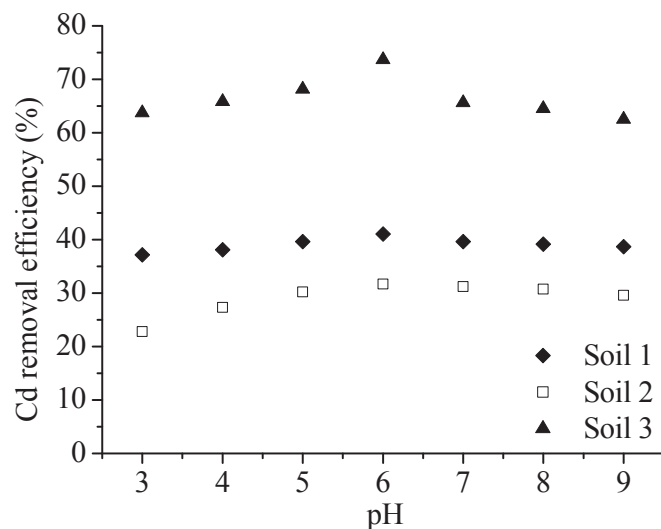


Fig. 4. The effect of solution pH on Cd removal efficiency. Experimental conditions: washing time: 12 h, liquid-solid ratio: 5, humic substance concentration: 3150 mg C/L.

30. Thus, it is possible to remediate Cd-contaminated soils to meet state requirement by a single washing with humic substances.

Although Cd removal efficiency increased with liquid-solid ratio, there was a trade-off between efficiency and treatment cost.

The higher the liquid-solid ratio, the more waste water was produced. A liquid-solid ratio of 5 was chosen to make practical operation in field cost-effective, by taking into account of water and energy consumption, machinery availability, and ease of effluent treatment.

3.4. Effect of pH on Cd removal efficiency

Fig. 4 shows that Cd removal efficiency was slightly greater at near neutral pH than at either the acidic or alkaline side of neutrality. This observation was in line with the effect of pH on the mobility of Cd and other heavy metals in soil (Sun et al., 2013, 2016; Cui et al., 2016). At pH 3, Cd removal efficiency was low, possibly because of reduced solubility of humic substances, and their partial precipitation onto soil (clay) particles. At low pH, the carboxylic groups of humic substances would also be less dissociated, while the humic substances molecules become more compact (Lamar et al., 2014; Kulikowska et al., 2015a). As a result, electrostatic interaction between humic substances and soil particles would increase as does humic substance precipitation/adsorption onto soil particles as Wang and Mulligan (2009) had observed for arsenic. Adsorption of humic substances onto soils is a common phenomenon (Simmler et al., 2013; Kulikowska et al., 2015a). At pH > 7, Cd removal efficiency decreased as Cd tends to form hydroxides and precipitate, making it more resistant to washing with humic substances. We have therefore chosen pH 6 as an acceptable operational condition.

3.5. Kinetics of Cd removal by humic substances

Fig. 5 shows that the amount of Cd removed from soils quickly increased with washing time before a plateau was reached at about 2 h. Thus, 2 h was chosen as a convenient soil washing time.

Data from the kinetic experiments were fitted into a pseudo-first- and pseudo-second-order model to describe the process of Cd desorption from soil and Cd adsorption (complexation) to humic substances.

Pseudo-first-order equation:

$$q_t = q_1(1 - e^{-k_1 t}) \tag{1}$$

Pseudo-second-order equation:

$$q_t = \frac{q_2^2 k_2 t}{1 + q_2 k_2 t} \tag{2}$$

where q_1 and q_2 are the amount of Cd adsorbed (mg/g) at equilibrium, q_t is the amount of Cd adsorbed at time t (mg/g), k_1 (1/h) and k_2 (g/(mg·h)) are the respective equilibrium rate constants.

In general, the pseudo-first-order model describes the initial kinetics process, whereas the pseudo-second-order model applies to the whole process of adsorption/desorption. The R^2 values in Table 2 indicate that Cd adsorption (complexation) to humic

substances (or Cd desorption from soil) was better described by the pseudo-second-order model, indicative of a chemisorption process (Ho and McKay, 1999).

3.6. Effluent treatment

As shown in Fig. 6, the wastewater from soil washing can be effectively treated with $\text{Ca}(\text{OH})_2$ to reduce Cd concentration to below the waste water discharge limit in China (0.1 mg/L). As the

Table 2

Parameters of kinetics of Cd migration from soils to washing agent humic substances.

Soil	pseudo-first-order			pseudo-second-order		
	q_1 (mg/g)	k_1 (L/h)	R_1^2	q_2 (mg/g)	k_2 (g/mg h)	R_2^2
Soil 1	0.55	4.6510	0.995**	0.56	28.4760	0.999**
Soil 2	2.23	3.5035	0.977**	2.32	3.3509	0.993**
Soil 3	1.63	5.7007	0.995**	1.66	13.5297	0.999**

**Significant at P = 0.01 level.

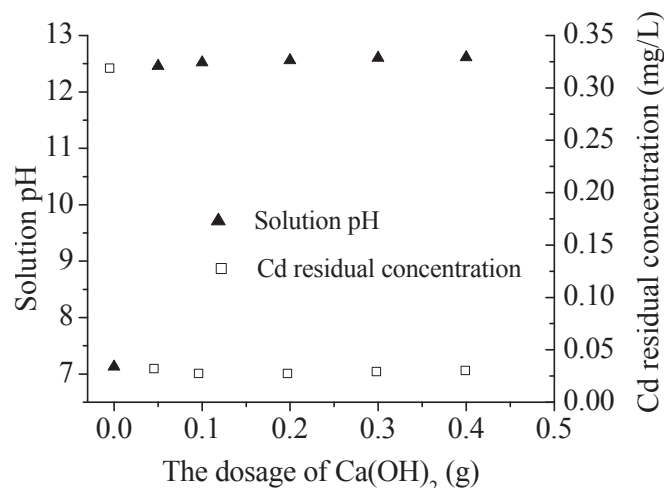


Fig. 6. The relationship between $\text{Ca}(\text{OH})_2$ dosage and Cd residual concentration and solution pH.

$\text{Ca}(\text{OH})_2$ dosage increased, effluent pH sharply increased from 7.13 to a plateau value of about 12.5. At the same time, there was a steep fall in Cd concentration from 0.32 to about 0.03 mg/L.

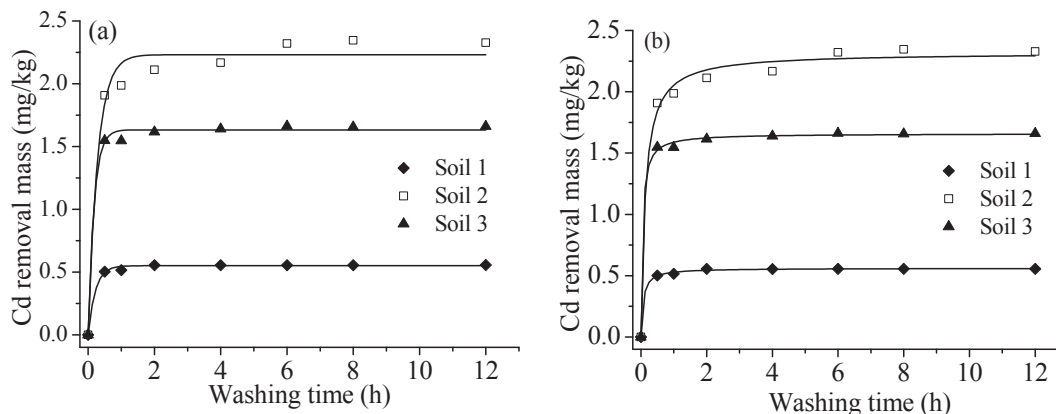


Fig. 5. Kinetics of Cd desorption from soils. (a)Pseudo-first-order equation (b) Pseudo-second-order equation. Washing conditions: solution pH: 6.0, liquid-solid ratio of 5, humic substance concentration: 3150 mg C/L.

Although $\text{Ca}(\text{OH})_2$ is only sparingly soluble in water (solubility product K_{sp} of 5.02×10^{-6}), the soluble component is fully ionized: $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$, leading to a high pH value. Thus, $\text{Ca}(\text{OH})_2$ played three roles in effluent treatment. First, its high pH made humic substances more effective in adsorbing Cd^{2+} and reduced free Cd^{2+} in effluent. Second, Ca^{2+} effectively flocculated almost all humic substances and their adsorbed Cd by forming a Cd-HS-Ca complex. Third, hydroxyl ions from $\text{Ca}(\text{OH})_2$ can combine with Cd to form a $\text{Cd}(\text{OH})_2$ precipitate (Baltpurvins et al., 1997). The treatment of waste water effluent with inexpensive $\text{Ca}(\text{OH})_2$ is an integral part of the humic substances-based washing technology for soil remediation.

3.7. Potential application of humic substances in soil remediation

Yuan (2008) and Makino et al. (2006) have proposed the following guidelines for assessing the suitability of washing agents for soil remediation: (1), these agents should be simple, effective and reliable allowing the contaminants in waste water to be recovered; (2), washing agents must be inexpensive; and (3), they must not be toxic to microbes, leach to groundwater, detrimental to soil structure and fertility, and harmful to plant growth.

Leonardite-derived humic substances apparently meet all of the above requirements (Senesi et al., 1991; Halim et al., 2003; Yuan and Theng, 2011). The humic substances in question contain only trace amount of heavy metals (Cd 0.16, Pb 9.59, Cu 12.49, Cr 8.73, As 6.41 Ni 13.93, Zn 37.56 mg/kg), far below the allowable metal concentration limit for farmland (The Ministry of Environmental Protection of People's Republic of China, 2006). Based on the trade-off between Cd removal efficiency and operational cost (e.g., time, water availability, and humic substances consumption), proper washing conditions can be determined to suit local soil properties, contamination levels, and remediation requirements. For the three contaminated soils used in this study, a combination of pH 6.0, a washing time of 6 h, liquid-solid ratio of 5, and a humic substances dosage of 3150 mg C/L could remove removed 42–75% of Cd in a single washing. Further, the Cd in the wastewater could readily be removed by adding a small dose of cheap $\text{Ca}(\text{OH})_2$ to meet effluent discharge requirements. Here we suggest field verifications of the washing method in two occasions. The first is to remediate Cd-contaminated paddy field where water is abundant and mixing soil and water is a normal practice in conjunction with fertilization and the transplantation of seedlings. Humic substances can be added to soil during the soil-water mixing operation. Removal of Cd from water can be done at drainage exit. The second is to remediate Cd-contaminated urban land for residential development, where the cost of remediation can be well justified, and the washing and effluent treatment can be done on site before the development.

4. Conclusions

Leonardite-derived humic substances have a low CMC and a great capacity to adsorb Cd. When used as a washing agent for Cd-contaminated soils, washing conditions may be tailored to suit soil properties and meet local remediation requirements. Using a humic substance concentration of 3150 mg C/L, a pH of 6.0, a washing time of 2 h, and a liquid-solid ratio of 5, a single washing could reduce the Cd concentration of three Cd-contaminated soils by 41.6, 36.8 and 74.9%. Further, the Cd concentration in the effluent (waste water) can be easily lowered to meet discharge requirements by treatment with a small dose of $\text{Ca}(\text{OH})_2$. Being superior to many washing agents in terms of washing effectiveness, safety, benefits to soil, and low cost, leonardite-derived humic substances have the potential to become the washing agent of choice for the

remediation of soils contaminated with Cd and other heavy metals. Paddy field with plenty of water or urban land with a high value could be chosen for a trial in the future.

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