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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.

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., $CaCl_2$, $FeCl_3$), strong acids (e.g., HCl, CH_3COOH), 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. $FeCl_3$ 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 ongoing 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 $Cd(NO_3)_2$ solution (12 mg Cd/L) at a solid:liquid ratio of 5 (g/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 $HCl:HNO_3$ 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).

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_2O)	–	6.57	6.16	5.51
Total Cd	mg/kg	1.33	6.57	2.63

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 $HClO_4:HNO_3:HF$ 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 $C_{14}H_{12}O_8$, 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