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Remediation of multiple heavy metal-contaminated soil through the combination of soil washing and in situ immobilization

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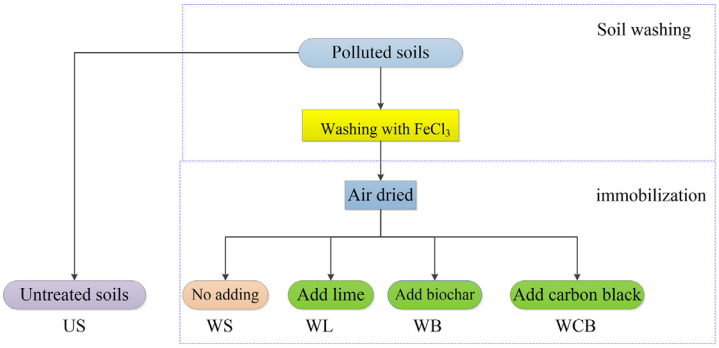
HIGHLIGHTS

- Soil washing combined with lime addition can effectively amend metal-polluted soil.
- pH is a crucial factor to control heavy metal lability in the combined remediation.
- Soil enzyme activities are greatly influenced by pH and acid-soluble metal contents.

GRAPHICAL ABSTRACT



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ABSTRACT

The remediation of heavy metal-contaminated soils is a great challenge for global environmental sciences and engineering. To control the ecological risks of heavy metal-contaminated soil more effectively, the present study focused on the combination of soil washing (with $FeCl_3$) and in situ immobilization (with lime, biochar, and black carbon). The results showed that the removal rate of Cd, Pb, Zn, and Cu was 62.9%, 52.1%, 30.0%, and 16.7%, respectively, when washed with $FeCl_3$. After the combined remediation (immobilization with 1% (w/w) lime), the contaminated soils showed 36.5%, 73.6%, 70.9%, and 53.4% reductions in the bioavailability of Cd, Cu, Pb, and Zn (extracted with 0.11 M acetic acid), respectively, than those of the soils washed with $FeCl_3$ only. However, the immobilization with 1% (w/w) biochar or 1% (w/w) carbon black after washing exhibited low effects on stabilizing the metals. The differences in effects between the immobilization with lime, biochar, and carbon black indicated that the soil pH had a significant influence on the lability of heavy metals during the combined remediation process. The activity of the soil enzymes (urease, sucrase, and catalase) showed that the addition of all the materials, including lime, biochar, and carbon black, exhibited positive effects on microbial remediation after soil washing. Furthermore, lime was the most effective material, indicating that low soil pH and high acid-soluble metal concentrations might restrain the activity of soil enzymes. Soil pH and nutrition were the major considerations for microbial remediation during the combined remediation. These findings suggest that the combination of soil washing and in situ immobilization is an effective method to amend the soils contaminated with multiple heavy metals.

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1. Introduction

According to a recently released survey by the Chinese Government, 16.1% of the soil samples collected from across the country has been polluted, and 82.4% of the polluted soil is contaminated by heavy metals or metalloids (Zhao et al., 2015). The sources of soil heavy metals are widespread, including industrial wastewater discharge, transportation and fertilizer application (Hou et al., 2017). To control and remedy soil pollution, a series of policies have been put forward by the Chinese Government (Hou and Li, 2017). Heavy metals in soil can damage the soil ecosystem, reduce the diversity of soil bio-communities, pose toxic effects on plants and reduce agricultural productivity. Furthermore, they can threaten human health through accumulation in food chain. Globally, heavy metal contamination of soil has threatened a considerable number of countries, including Europe (Jarup, 2003), Brazil (Franca et al., 2017), the USA (Uchimiya et al., 2011), and Japan (Makino et al., 2006).

Mobilization and immobilization treatments are the two main methods employed nowadays to remediate soil heavy metal pollution (Bolan et al., 2014). These include phyto-extraction (Jiang et al., 2010; Jiang et al., 2003; Liu et al., 2009; Van Nevel et al., 2007), soil washing (Beiyuan et al., 2017; Dermont et al., 2008; Mulligan et al., 2001; Wei et al., 2016), and in situ immobilization (Cao et al., 2008; Haidouti, 1997; Lombi et al., 2003; Porter et al., 2004). Phyto-extraction refers to the removal of heavy metals using plants as accumulators, which usually requires a long time and is not suitable for limited farmland area. Soil washing can remove a certain amount of metals from soils by dissolving heavy metals in the eluant (Dermont et al., 2008). The soils after proper washing can be reused, which can have both social and economic benefits (Hou et al., 2015; Hou et al., 2014). However, a large number of heavy metals and a portion of leachate remain in soils after washing. Furthermore, the bioavailability of the residual heavy metals can be significantly influenced by acid rain. Ferric chloride ($FeCl_3$) can remove metals via several ways: the competition for adsorption sites through H^+ and Fe^{3+} ions and the formation of soluble complexes by Cl^- ion. It has a better cadmium (Cd) removal performance than some acids, such as HCl, HNO_3, and H_2SO_4 (Makino et al., 2008). Furthermore, as Fe and Cl are important constituents of soils, the effect of ferric chloride on soil might be relatively low. Studies have shown that 6%–20% of heavy metals in the topsoil can be removed through $FeCl_3$ washing during field experiments; however, acid rain can influence the bioavailability of the remnant metals (Guo et al., 2016).

Unlike soil washing, the main goal of in situ immobilization is to decrease the mobility and bioavailability of heavy metals; however, the total amount of heavy metals in soil is not reduced. Lime (Derome, 2000; Lombi et al., 2003; Mallampati et al., 2012) and biochar (Lu et al., 2012; Tang et al., 2013; Zhang et al., 2013) are the common materials that have been tested effectively to stabilize heavy metals. In situ field experiments have shown that both lime and biochar can lower the uptake of heavy metals by plants and improve their biomass to some extent (Cui et al., 2016a; Cui et al., 2016b; Lee et al., 2009; Liu et al., 2013). Studies have also reported that lime can be used to remediate soils polluted with metals (Hou et al., n.d.; Tan et al., 2011), whereas the application of biochar has been limited to fields (O'Connor et al., 2018). With larger specific surface area and more functional groups than biochar (Donnet and Lansinger, 1992), carbon black as a sorbent can also be used to amend polluted soils (Park et al., 2013; Zhou et al., 2010).

Earlier studies have mainly focused on only soil washing or in situ immobilization to amend contaminated soils (Makino et al., 2016; Shen et al., 2018), which ignored their respective disadvantages. The combination of soil washing and in situ immobilization is beneficial as it exploits their advantages and compensates for their respective deficiencies. In this study, we investigated the combined effect of soil washing (with $FeCl_3$) and in situ immobilization (with lime, biochar and carbon black) to remediate the soil contaminated with multi metals. In addition, we analysed the changes in heavy metal (total and bioavailable metals) contents, soil properties and soil enzymes activities after the combined effect. Our focus was to control the risk of heavy metal contamination and develop an effective remediation strategy through this method.

2. Materials and methods

2.1. Materials

Lime (analytical pure) was purchased from the Sinopharm Chemical Reagent Co., Ltd., China. Biochar was derived using rice straw, which was pyrolyzed for 1 h at 450 °C with nitrogen. Carbon black was procured from the Shanghai Haofu Chemical Industry, China. After incomplete combustion of the natural gas, the carbon black was passed through a special nozzle and deposited on the channel surfaces for collection. It usually contains a large specific surface area and less ash. With a high content of functional oxygen groups, this type of black carbon acts as a chemical acid.

2.2. Soil sampling

The soil sample was collected from the plough layer (0–20 cm deep) of a paddy field (derived from the Quaternary red clay and modern floodplain sediments) near a smelter (27°52′34″N, 113°04′54″E). The smelter has caused severe soil contamination with mercury (Hg), lead (Pb), zinc (Zn), Cd, copper (Cu) and arsenic (As) (Li et al., 2011b). Among these, Pb, Zn, Cd and Cu are the main contaminants as their concentrations are significantly higher than the environmental quality standard of China. After sampling, the soil was air-dried at room temperature (25 ± 2 °C) and passed through a 2-mm sieve. The soil pH was measured using the HI 3221 pH meter (Hanna instruments Inc., USA) with a soil/water ratio of 1:2.5 (Huang et al., 2014); soil organic matter (SOM) content was determined by the potassium dichromate ($K_2Cr_2O_7$) digestion method (Zhang et al., 2017); dissolved organic matter (DOC) content was determined using the total organic carbon analyzer (Shimadzu, Japan); cation exchange capacity (CEC) was measured by the barium chloride ($BaCl_2$) displacement method (Wang et al., 2015). The soil texture was analysed according to Ball (1964). Total Pb, Cu, Zn and Cd contents in soil were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) after mixed acid (HNO_3-$HClO_4$-HF) digestion (Li et al., 2016). The major physicochemical characteristics of the soil before and after washing are presented in Table 1.

2.3. Soil washing treatment

To determine the best washing condition, 3 g of contaminated soil was mixed with different $FeCl_3$ concentrations (0–1 M) and washing liquid/soil ratios (1.2–10), the mixtures were vibrated at room temperature (25 ± 2 °C) for 1 h. The content of heavy metals (Cd, Cu, Zn and Pb) dissolved in the supernatant was measured by ICP-OES after

Table 1
The major physicochemical characteristics of the soil before and after washing.

Variables/properties and units	Before	After
Clay (%)	32.81 ± 0.04	37.90 ± 0.66
Silt (%)	43.27 ± 3.43	44.55 ± 1.80
Sand (%)	23.92 ± 3.48	17.56 ± 1.02
pH	5.24 ± 0.03	3.69 ± 0.06
Soil organic matter (%)	38.43 ± 0.59	40.90 ± 0.84
CEC(cmol/kg)	21.50 ± 1.00	15.83 ± 0.29
Cd (mg/kg)	18.33 ± 0.29	6.8 ± 0.1
Pb (mg/kg)	461.37 ± 2.65	220.97 ± 2.25
Cu (mg/kg)	175.47 ± 2.55	146.23 ± 0.60
Zn (mg/kg)	1182.63 ± 1.69	827.53 ± 3.89