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A combination of ferric nitrate/EDDS-enhanced washing and sludge-derived biochar stabilization of metal-contaminated soils

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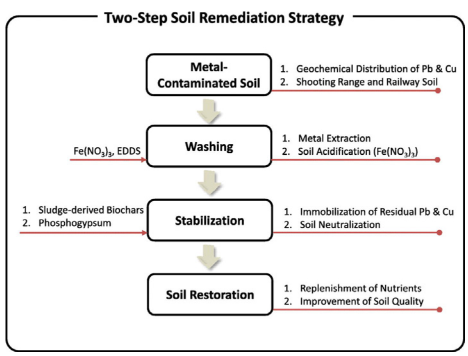
HIGHLIGHTS

- $Fe(NO_3)_3$ washing significantly removed Pb from shooting range and railway soils.
- Biochars neutralized acidic soil pH resulting from $Fe(NO_3)_3$ washing.
- Phosphogypsum immobilized residual Pb by forming insoluble $PbSO_4$ precipitates.
- Sludge-derived biochars reduced metal mobility and enhanced soil quality.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, soil washing and stabilization as a two-step soil remediation strategy was performed to remediate Pb- and Cu-contaminated soils from shooting range and railway sites. Ferric nitrate ($Fe(NO_3)_3$) and [*S,S*]-ethylenediamine disuccinate (EDDS) were used as washing agents, whereas three types of sludge-derived biochars and phosphogypsum were employed as soil stabilizers. While $Fe(NO_3)_3$ extracted larger amounts of metals compared to EDDS (84% Pb and 64% Cu from shooting range soil; 30% Pb and 40% Cu from railway site soil), it caused severe soil acidification. Both $Fe(NO_3)_3$ and EDDS washing enhanced the mobility of residual metals in the two soils, which in most cases could be mitigated by subsequent 2-month stabilization by sludge-derived biochars or phosphogypsum. By contrast, the metal bioaccessibility could only be reduced by soil washing. Nutrient-rich sludge-derived biochar replenished available P and K in both soils, whereas $Fe(NO_3)_3$ washing provided available nitrogen (N). Soil amendment enhanced acid phosphatase activity but marginally improved soil dehydrogenase and urease activity in the treated soils, possibly due to the influence of residual metals. This study supported the integration of soil washing (by $Fe(NO_3)_3$ or EDDS) with soil stabilization (by sludge-derived biochars

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or phosphogypsum) for accomplishing the reduction of metal mobility and bioaccessibility, while restoring the environmental quality of the treated soils.

1. Introduction

Excessive accumulation of heavy metals in edible crops grown in contaminated soils leads to chronic human health problems. Ex-situ soil washing extracts contaminants from the soils with relatively higher remediation efficiency, shorter treatment time, and better cost-effectiveness compared to in-situ extraction techniques (Wei et al., 2016). However, the washing agents should be selected thoughtfully in view of the contamination characteristics of soils. Vast research studies have focused on biodegradable chelating agents, cationic salts, and low-molecular-weight organic acids, which incur less adverse impact on the soil quality compared to strong acids (e.g., mineral dissolution, nutrient loss, soil disintegration) (Begum et al., 2012; Kim and Baek, 2015; Makino et al., 2008). Among them, ferric nitrate/chloride salts and [*S,S*]-ethylenediamine disuccinate (EDDS) showed promising removal efficiencies of Pb and Cu from contaminated soils/sediments (Race et al., 2016; Yoo et al., 2013). This is because hydrolysis of ferric salts produces large amounts of hydrogen ions while EDDS forms stable metal-EDDS complexes to enhance metal solubilization. However, soil acidification increased the amount of water-soluble metals, especially for Pb (Isoyama and Wada, 2007), while chelant-enhance washing also increased mobility of residual metals in soils (Tsang and Hartley, 2014; Beiyuan et al., 2016). Besides, there was little information about the influence of ferric salt washing on the metal mobility/bioaccessibility/phytoavailability, soil nutrients, and enzyme activities in the treated soils.

In-situ stabilization with suitable soil amendments can be applied for contaminant immobilization (Bolan et al., 2014; Tsang and Yip, 2014), among which biochar has been popular as it can concurrently improve soil quality by enhancing water holding capacity, adjusting soil pH, increasing microbial population and plant growth (Ahmad et al., 2017; Igalavithana et al., 2017). Our recent studies showed that integrating EDDS washing with subsequent soil stabilization by biochar could reduce the leachability and bioaccessibility of residual metals in e-waste recycling site and timber treatment site soils (Beiyuan et al., 2016; Beiyuan et al., 2018). It is widely recognized that stabilization performance of biochars are highly dependent on the feedstock materials and pyrolysis conditions (temperature, retention time, and heating rate) (Ahmad et al., 2014; Uchimiya et al., 2011). In particular, stable Pb precipitation and increased crop production could be accomplished by soil amendment with phosphate minerals (Cao et al., 2008; Cao et al., 2009) and phosphogypsum (industrial waste) (Anikwe et al., 2016; Yan et al., 2016). Similarly, soil amendment with dairy manure biochar (Cao et al., 2011) and sewage sludge biochar (Fang et al., 2016) could reduce the metals/metalloids mobility and improved agronomic properties of contaminated soils, because of high contents of mineral oxides, phosphate, and carboxylic groups (Zhang et al., 2017; Wang et al., 2017). Thus, this study proposed a post-washing stabilization by sludge-derived biochar and waste phosphogypsum to mitigate the increased mobility/bioaccessibility of residual metals and ameliorate the compromised soil quality due to $Fe(NO_3)_3$ and EDDS washing of Cu- and Pb-contaminated shooting range and railway site soils.

In this study, sludge obtained from three different types of sewage treatment works in Hong Kong (i.e., non-saline secondary treatment, saline secondary treatment, and saline chemically-enhanced primary treatment) were used as feedstock for biochar production and characterization. Then, the efficacy of removal/stabilization of two different contaminated soils by $Fe(NO_3)_3$/EDDS washing followed by sludge-derived biochar/phosphogypsum stabilization was assessed in terms of mobility, bioaccessibility, and phytoavailability of residual Cu and Pb, available nutrients, and soil enzyme activities.

2. Materials and methods

2.1. Characterization of soil samples, biochars, and phosphogypsum

Two field-contaminated soil samples from shooting range (military site) and railway corridor (37°31′47″ N 126°57′52″ E) were collected from Korea, air-dried and sieved through 2 mm, and their physicochemical characteristics are shown in Table 1. Particle size distribution, water holding capacity, soil organic matter, cation exchange capacity were determined for the two soils by standard methods (Supplementary Information). Available N as the sum of NH_4-N and NO_3-N in the soil was determined by 2 M KCl extraction method (Paul et al., 2010). Available P as PO_4-P in the soil was determined by Bray's extraction method (Bray and Kurtz, 1945). Available K was extracted by 1 N sodium acetate (NaOAc) solution at a liquid-to-soil ratio of 10 L g^{-1} (Jo et al., 2012).

Soil mineralogy was analyzed using X-ray diffraction (XRD, D/MAX-2500, Rigaku, Japan). The abundant soil minerals in both soils were quartz (SiO_2), muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$), and kaolinite ($Al_2Si_2O_5(OH)_4$). In shooting range soil, cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) were clearly observed as Pb sources. It was reported that Pb can exist as an easily bioavailable form of $PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$ in shooting range soil (Cao et al., 2008). The surface morphology and elemental mapping of the samples was investigated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX, TESCAN VEGA3 XM, Czech Republic). Besides, metals in soil were extracted in *aqua regia* solution and analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent, 720-ES, USA). The geochemical distribution of heavy metals in the soils (Table 1) was determined by Standards, Measurements and Testing Programme (SMT) sequential extraction method categorizing metals into four fractions: soluble and exchangeable fraction (Fraction 1), Fe/Mn oxides fraction (Fraction 2), organic matter and sulfides fraction (Fraction 3), and residual fraction (Fraction 4) (Quevauviller et al., 1997).

Three types of biochars were produced by a mixture of sewage sludge and waste sawdust at a 1:1 mass ratio. The sawdust (masson pine with particle size smaller than 0.6 mm) was added to provide desirable physical properties. The sludge samples were collected from three typical wastewater treatment plants in Hong Kong, i.e., freshwater sludge after secondary treatment from Shek Wu Hui (SWH) sewage treatment works, saline sludge after secondary treatment from Taipo (TP) sewage treatment works, and saline sludge after chemically enhanced primary treatment (CEPT) from Stonecutters Island (SI) sewage treatment works. This is because 80–85% coverage of Hong Kong adopts seawater for toilet flushing, which allows comparison of a wide range of representative properties of sludge-derived biochars from different sources and treatment levels. The sludge samples were oven-dried (60 °C) and passed through a 2-mm sieve. Homogeneous blend of sludge and sawdust was transferred into a computer-controlled furnace at a constant heating rate of 10 °C min^{-1} to reach 300 °C and maintained for 1 h with 1.5 L min^{-1} dry nitrogen gas. It was allowed to cool down in nitrogen gas purging until 100 °C. The phosphogypsum consisted of 86.6 wt% $CaSO_4 \cdot H_2O$, which was a by-product from phosphoric acid production obtained from Hubei, China. The density of phosphogypsum was 0.81 g cm^{-3} and its particle size ranged from 5 to 15 μm. To characterize the three types of sludge-derived biochar, pH values, BET surface area,