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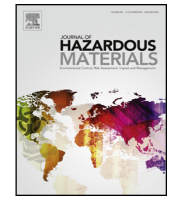

Enhancing the soil heavy metals removal efficiency by adding HPMA and PBTCA along with plant washing agents

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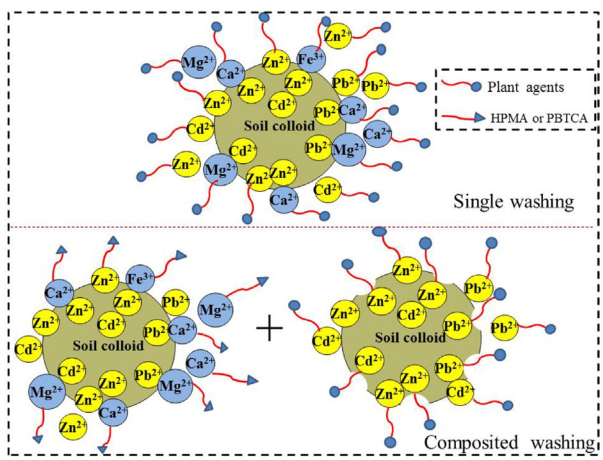
HIGHLIGHTS

- Soil metals were effectively removed by plant agents with HPMA or PBTAC.
- The addition of HPMA and PBTCA greatly enhance the soil metal removals.
- The adverse effects of soil properties were lower by composited washing than by EDTA.

GRAPHICAL ABSTRACT



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ABSTRACT

Plant washing agents—water-extracted from *Coriaria nepalensis* (CN), *Clematis brevicaudata* (CB), *Pistacia weinmannifolia* (PW) and *Ricinus communis* (RC)—are feasible and eco-friendly for soil heavy metal removal, but their single application has limited removal efficiency. To improve their metal removal efficiencies, two biodegradable assistant agents, hydrolytic polymaleic anhydride (HPMA) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA), were investigated in combination with plant washing agents through batch soil washing experiments. Results showed that the addition of HPMA or PBTCA with plant agents greatly enhanced the removal efficiencies of soil heavy metals ($p < 0.05$). Under acidic conditions, the maximum improvements in soil heavy metal removal reached 18.69% and 18.00% for soil Cd and Zn by PW + HPMA, respectively, and 12.89% for soil Pb by CN + HPMA. Under neutral or alkaline conditions, the largest improvements in soil Cd, Pb and Zn were 24.18%, 54.38% and 25.47% by PW + PBTCA, respectively. When compared with EDTA, the loss rates of soil nitrogen, phosphorus and potassium significantly decreased ($p < 0.05$) and the soil organic carbon significantly increased ($p < 0.05$) after washing with the combinations. Hence, the addition of HPMA or PBTCA with the plant agents could improve the removal of soil heavy metals.

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1. Introduction

Soil contamination with heavy metals derived from various anthropogenic activities [1], including agricultural practices, industrial [2] and mining activities [3], has been one of the major environmental problems throughout the world [4]. Among these heavy metals, cadmium (Cd), lead (Pb) and zinc (Zn) contribute the major share of soil contamination because they are non-biodegradable and highly persistent in the soil environment [5,6]. Additionally, they can accumulate in living organisms [7] and cause harmful effects to plants, animals and human beings through food chain transfers [8,9]. Therefore, it is imperative to remediate soils contaminated with Cd, Pb and Zn.

At present, metal-contaminated soils have been treated with several remediation technologies [10] such as soil replacement or filling [11], electrodialysis [12], soil washing [13] and phytoremediation [14]. Among them, soil washing is considered as one of the few effective treatment alternatives for the remediation of heavy metal contaminated soil because it can permanently separate metals from soils in a short period [15]. In the literature, various washing agents (acids, surfactants, chelating agents, salts, or redox agents) have been tested [15]. Unfortunately, although these agents have been demonstrated to be effective in removing heavy metals [10,16–19], they can have some drawbacks. For example, strong acids could cause important losses of soil mineral substances and organic matter [20,21], and some agents could be expensive or cause secondary pollution [15,22,23]. Therefore, efforts should be directed towards the development of low-cost and environmentally friendly washing agents for the restoration of heavy metal contaminated soils.

A previous study demonstrated that soil washing agents water-extracted from *Coriaria nepalensis* (CN), *Clematis brevicaudata* (CB), *Pistacia weinmannifolia* (PW) and *Ricinus communis* (RC) [24] could be feasible for heavy metal removal. As natural products, they could be biodegradable in the environment and might be more promising, eco-friendly and less disruptive for contaminated soils. However, single application of these plant agents has limited removal efficiency. Consequently, there is a need to use some additional agents to enhance the removal efficiency of Cd, Pb and Zn by the plant agents.

Hydrolytic polymaleic anhydride (HPMA) and 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) are two kinds of biodegradable assistant agents [25,26]. They were beneficial to improve the metal removal in our preparatory experiment. Currently, no studies have investigated their use to improve the washing of soil heavy metals with plant washing agents.

We hypothesize that HPMA and PBTCA are potential assistant agents to enhance the soil Cd, Pb and Zn removal efficiencies during soil washing by incorporation with plant agents. The purposes of the present study were: (1) to investigate whether the addition of HPMA or PBTCA could enhance or reduce the removal efficiencies of soil Cd, Pb and Zn; (2) to evaluate the effect of concentration of plant agents, solution pH and contact time with addition of HPMA or PBTCA on metal removal; and (3) to compare the changes in soil chemical properties after soil washing with various washing treatments.

2. Materials and methods

2.1. Soil sampling preparation

The metal-contaminated soil sample was derived from a waste farmland in the vicinity of the Tangjia Pb-Zn Mine in Hanyuan, Sichuan (29°24′N, 102°37′E); the soil type is Typic Calcaric Purpli-Udic Cambosols and the heavy metal contents are consistent with the degree of soil heavy metal pollution in the area. The experimental soil is sandy clay with clay, silt and sand contents of 63.7%, 11.2% and 25.1%, respectively, and the soil Cd, Pb and Zn contents were 16.15, 706.93 and 1603.43 mg kg^{-1}, respectively. The soil was collected from the 0–20 cm layer and air-dried to grind through a 2-mm screen before being homogenized for the experiments. Total Cd, Pb and Zn in the soil was measured by atomic absorption spectrophotometer (AAS, Thermo Solaar M6, Thermo Fisher Scientific Ltd., USA) after digesting the sample with a HNO_3/HCl/$HClO_4$ solution at a ratio of 1:2:2 (v/v/v).

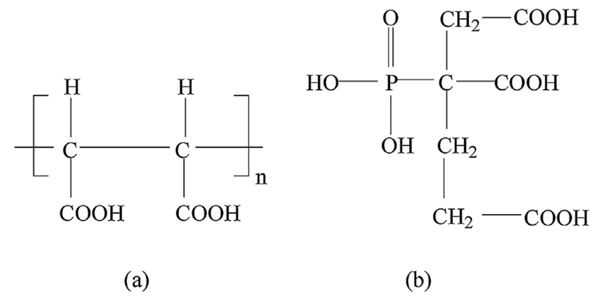

Fig. 1. Structures of HPMA (a) and PBTCA (b). (HPMA, 0.1 M hydrolytic polymaleic anhydride; PBTCA, 0.1 M 2-phosphonobutane-1,2,4-tricarboxylic acid).

2.2. Washing materials

The plant washing agents were lixiviated by distilled water from four plant materials including CN, CB, PW and RC. Their extraction processes were reported in our previous studies [27], and their concentrations were expressed as the initial mass of plant powder and the volume of the distilled water.

Biodegradable assistant agents HPMA (product no. 26099-09-02) and PBTCA (product no. 37971-36-1) were purchased commercially (Shangdong Taihe Water Treatment Technologies Co., Ltd, China). Their purities are 48% and 50%, respectively, and their structures are shown in Fig. 1 [25,28].

2.3. Experimental design

Two types of soil washing solutions were used in this study: (1) mixed solution of plant washing agents and HPMA (CN + HPMA, CB + HPMA, PW + HPMA and RC + HPMA); and (2) mixed solution of plant washing agents and PBTCA (CN + PBTCA, CB+ PBTCA, PW+ PBTCA and RC+ PBTCA). The mixed solution was based on our preparatory experiment and was prepared by adding the HPMA or PBTCA to plant washing solutions to result in an intermixture comprising 0.1 M HPMA or PBTCA individually. Concentrations of Pb and Zn in the mixed washing solution were 0.06 and 0.10 mg L^{-1} respectively (Cd was not detected). Soils (2.00 g) mixed with washing solution (40.00 mL) were shaken by a mechanical shaker at 150 rpm in acid-rinsed polycarbonate plastic bottles (50 mL) for a specific period of time. All solutions were prepared with distilled water.

Experiments were performed under different washing conditions including variation in the concentration of plant agents, solution pH and contact time: (1) The effect of the concentration of plant agents (20–80 g L^{-1}) on metal removal was studied at pH 4.0 with 120 min contact time; (2) Experiments assessing solution pH (3.0–9.0) on metal removal were conducted with 50 g L^{-1} plant agents and 120 min contact time; and (3) The kinetic study was performed with 50 g L^{-1} plant agents and pH 4.0 for various contact times (5–240 min). The pH values of the reaction systems were adjusted with dilute HNO_3 or NaOH. After shaking was completed, the suspensions were immediately centrifuged at 3000 rpm for 5 min, and the supernatants were analyzed for heavy metals by