

Removal of Pb, Zn, and Cd from contaminated soil by new washing agent from plant material

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Abstract Soil washing is an effective approach to remove soil heavy metals, and the washing agent is generally regarded as one of the primary factors in the process, but there is still a lack of efficient and eco-friendly agents for this technique. Here, we showed that four plant washing agents—from water extracts of *Coriaria nepalensis* (CN), *Clematis brevicaudata* (CB), *Pistacia weinmannifolia* (PW), and *Ricinus communis* (RC)—could be feasible agents for the removal of soil lead (Pb), zinc (Zn), and cadmium (Cd). The metal removal efficiencies of the agents increased with their concentrations from 20 to 80 g L⁻¹, decreased with the increasing solution pH, and presented different trends with the reaction time increasing. CN among the four agents had the highest removal efficiencies of soil Pb (62.02%) and Zn (29.18%) but owned the relatively low Cd removal efficiencies (21.59%). The Fourier transform infrared spectroscopy showed that the abilities of plant washing agents for the removal of soil heavy metals may result from bioactive substances with specific functional groups such as –COOH, –NH₂, and –OH. Our study provided CN as the best washing agents for the remediation of contaminated soil by heavy metals.

Keywords Plant washing agent · Heavy metal · *Coriaria nepalensis* · Influence factor · FTIR

Introduction

Soil contamination with heavy metals has become a world-wide concern due to the intensification of human activities such as mining, smelting, and electroplating in recent years (Jho et al. 2015; Morcillo et al. 2016; Tai et al. 2013). Some heavy metals like lead (Pb) and cadmium (Cd) have high toxicity to human health (Nogawa et al. 2004; Sone et al. 2009), while others such as zinc (Zn) are indispensable at low concentrations but harmful in excessive quantities for creatures (Touceda-González et al. 2015). In addition, these heavy metals are hazardous and persistent in soils (Han et al. 2016; Wu et al. 2015). Consequently, there is an urgent need to remediate the soils contaminated by Pb, Zn, and Cd.

Several remediation techniques including stabilization (Bosio et al. 2014), electrodialysis (Gherasim et al. 2014), and phytoremediation (Zhang et al. 2013) have been widely applied to repair heavy metal-polluted soils. Although these methods could be useful, they have been demonstrated to be costly or time-consuming (Wang et al. 2014). To the contrary, soil washing is considered as one of the most promising methods to remove soil heavy metals due to its time-saving and cost-efficient properties and being applicable to multiple contaminants (Im et al. 2015; Satyro et al. 2016; Yi and Sung 2015).

Soil washing is a chemical extraction technique based on the desorption of pollutants from contaminated soils via various agents (Kulikowska et al. 2015). Many researchers have investigated the effects of different types of washing agents on the removal efficiency of soil heavy metals. For example, Moon et al. (2012) reported that 56.7% Zn was removed by hydrochloric acid (HCl). Nevertheless, strong acids can result

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in soil matrix destruction due to excessive acidification (Ko et al. 2005). Although several studies have shown that ethylenediaminetetraacetic acid (EDTA) is effective in removing heavy metals from contaminated soil (Cui et al. 2015; Pocięcha and Lestan 2010; Voglar and Lestan 2012, 2013; Zupanc et al. 2014), it may cause a secondary pollution for its toxicity and the long persistence in soil environment (González et al. 2011). Therefore, it is essential to search new feasible eco-friendly washing agents for the remediation of metal-contaminated soils.

The plant material is cost-effective and eco-friendly due to extensive sources and strong biodegradability. Currently, although many lines of research have devoted to studying the saponin derived from soapberry as natural plant-based surfactant for the removal of soil heavy metals (Gusiatin and Klimiuk 2012; Maity et al. 2013a; Maity et al. 2013b), rather, less attention has been paid to investigating washing agents extracted from other plants to remove heavy metals. Hence, screening new plant material may be of great significance.

Coriaria nepalensis, *Clematis brevicaudata*, *Pistacia weinmannifolia*, and *Ricinus communis* are all perennial plants and extensively distributed in China (Zeng et al. 2007; Zhao et al. 2005; Zhao et al. 2012). Additionally, Hao et al. (2013), Ohishi et al. (2014), Yang et al. (2011), and Zhao et al. (2005) have reported that they have carboxyl or hydroxyl in their components. Therefore, we may speculate that they may chelate with heavy metal ions in soils. The results of our preliminary experiment indicated that they could remove heavy metals from contaminated soils to some extent, but a systemic study is lacking. The objectives of this study were (1) to test the effects of concentration, pH, and washing time on soil Pb, Zn, and Cd removal and (2) to identify the participant functional groups on the plant washing agents during soil washing.

Materials and methods

Soil sampling and characterization

The contaminated soil was collected from the surface layer (0–20 cm) of a waste farmland in Tangjia Pb-Zn Mine in Hanyuan, Sichuan (29° 24' N, 102° 37' E). Samples were air-dried and sieved to 2 mm. Soil pH was measured in a 1:2.5 (w/v) soil/deionized water suspension. Soil samples were analyzed for organic carbon by Walkley-Black titrations (Nelson and Sommers 1996). Total nitrogen in soil was determined by the Kjeldahl method (Bremner and Sparks 1996), and available phosphorus was extracted using 0.5 M NaHCO₃ (pH = 8.5) and measured by the molybdenum antimony colorimetry method (Olsen and Sommers 1982). Soil texture was analyzed by the pipette method (Gee and Bauder 1986). The contaminated soil was digested in a solution mixed with

HNO₃-HCl-HClO₄ in a 1:2:2 ratio (v/v/v). Concentrations of Pb, Zn, and Cd in the contaminated soils were measured by flame atomic absorption spectrometry (AAS, Thermo Solaar M6, Thermo Fisher Scientific Ltd., USA).

Preparation of plant washing solutions

The overground part of plants including *C. nepalensis* (CN), *C. brevicaudata* (CB), *P. weinmannifolia* (PW), and *R. communis* (RC) was selected based on our preliminary experiments and obtained in Hanyuan, Sichuan. The plant samples were collected and washed thoroughly with running tap water followed by deionized water before being dried at 65 °C for 72 h and then ground by a grinder (DFY-500, Wenling Linda Machinery Co., China) and passed the 2-mm sieve. The plant powders were oscillated for 24 h by distilled water at 25 °C under 150 rpm and thereafter filtered for plant washing agents. The agent concentrations were expressed by the initial mass of plant powder and the volume of the distilled water. Concentrations of Pb, Zn, and Cd in the plant materials were determined by AAS (Thermo Solaar M6, Thermo Fisher Scientific Ltd., USA).

Soil washing experiments

Batch experiments about the four plant agents were carried out in different washing conditions including the concentrations, solution pH, and washing time. All the soil washing experiments were conducted in 50-mL-capacity polyethylene tubes with soils (2.00 g) to washing solution (40 mL) at a solid/liquid ratio of 1:20 (w/v). The samples were then shaken in a mechanical shaker at 150 rpm at room temperature (25 °C) for a period. At the end of the extraction, the suspensions were immediately filtered through a 0.45 μm filter membrane. The concentrations of Pb, Zn, and Cd in the filtrate were measured by AAS. All tests were conducted in triplicate.

Concentrations

Each plant washing agent was prepared in concentrations of 20, 35, 50, 65, and 80 g L⁻¹. Then, the washing solutions were pipetted into soils in 50-mL-capacity polyethylene tubes and the intermixture with HNO₃ or NaOH was adjusted at pH 4.0. The samples were oscillated at 150 rpm for 2 h at 25 °C in a shaker. Afterwards, the suspensions were immediately filtered for determination of heavy metals. At this pH condition, the soil values after washing were 6.1–6.7.

pH

Each plant washing agent at the concentrations of 50 g L⁻¹ was added into soils in 50-mL-capacity polyethylene tubes, and the pH values of the reaction systems were adjusted at 3.0,

4.0, 6.0, 7.0, and 9.0. Next, the samples were shaken on a shaker at 150 rpm for 2 h at 25 °C. The suspensions were immediately filtered for determination of heavy metals.

Washing time

Kinetic experiments were conducted at the time of 0.5, 1.0, 1.5, 2.0, and 4 h in the concentrations of each reagent with 50 g L⁻¹ at pH 4.0 in 50-mL-capacity polyethylene tubes. The samples were stirred at 150 rpm at 25 °C in a shaker. The suspensions were immediately filtered for determination of heavy metals.

FTIR analysis of plant agents before and after soil washing

In order to identify the participant functional groups on the plant washing agents during the soil washing process, the plant agents before and after washing were dried at 40 °C and analyzed by an FTIR spectrophotometer (Spectrum Two, PerkinElmer Inc., USA). The agents after soil washing were collected at concentrations of 50 g L⁻¹ at pH 4.0 for 2 h. The materials were ground with KBr sufficiently in the agate mortar at a ratio of 1:200 and pressed into a disk under high pressure. The spectra were recorded from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹.

Changes of heavy metal fractions by soil washing

The soils washed with 50 g L⁻¹ plant washing agents after 2 h of reaction at 1:20 w/v and an initial pH 4.0 were collected. The distribution of metal fractions including exchangeable, reducible, oxidizable, and residual fractions in the contaminated soil before and after washing was determined by the modified Community Bureau of Reference (BCR) three-step sequential extraction procedure (Pueyo et al. 2008).

Quality control and statistical analysis

Standard reference material (GBW07405) was used for analyzing the accuracy and precision of the analytical method (accuracies within ±5%) during the digestion procedure. SPSS Version 19.0 (SPSS Inc., Chicago, Ill, USA) was used for data statistical analysis. Differences in Pb, Zn, and Cd removal efficiency among different experimental conditions were identified by one-way ANOVA. Mean values were compared by least significant difference and if $p < 0.05$ were considered to indicate significance.

Results and discussion

Characters of soil sample and plant agent

The texture of metal-contaminated soil was sandy clay with 63.7% sand, 11.2% silt, and 25.1% clay, respectively. Soil organic carbon, total nitrogen, available phosphorus, and pH were 19.7 g kg⁻¹, 1.1 g kg⁻¹, 21.9 mg kg⁻¹, and 7.23, respectively. The concentrations of soil Pb, Zn, and Cd were 698.72, 1587.27, and 15.05 mg kg⁻¹, respectively, and substantially exceed the threshold of farmland (The China Environmental Quality Standard for soils, GB 15618-1995). The pH values of plant agents were 5.8–6.6, and the concentrations of Pb and Zn in plant agents (80 g L⁻¹) were 0.04 and 0.07 mg L⁻¹, respectively (Cd was not detected).

Effect of concentrations on the removal of soil Pb, Zn, and Cd

The concentration of washing agent is essential to soil washing, as it determines the amount of substance which will involve in the reaction (Chen et al. 2016). In order to investigate the effect of concentrations of the agents on removal of soil heavy metals, four plant agents with different concentrations were used in the experiments. As shown in Fig. 1, their removal efficiencies of soil Pb, Zn, and Cd presented a logarithmic increase with increasing concentrations from 20 to 80 g L⁻¹. The results suggest that higher concentrations of plant agents lead to more effective removal of heavy metals. This may be ascribed that the agents derived from plants may have functional groups such as carboxyl or hydroxyl, which can form complex with heavy metals (Cao et al. 2013; Song et al. 2008). Therefore, the higher concentration of agents could bind to more heavy metal ions due to more active substances. Similar results were observed with saponin derived from plant for the washing of soil heavy metals at different concentrations (Maity et al. 2013b). Among the agents, CN had the highest removal efficiencies for soil Pb (62.02%) and Zn (29.18%) at the concentration of 80 g L⁻¹ (Fig. 1a, b), but the maximum Cd removal efficiency by CN was only 21.60% and significantly lower than those of CB and RC at the same concentration ($p < 0.05$). In contrast, the latter two agents had the higher Cd removal efficiencies with 25.89 and 25.24%, respectively (Fig. 1c). However, PW had the lowest removal efficiencies for the metals from the soil. Kim et al. (2016) have reported that the removal of soil heavy metals not only depends on the type of metals and their concentrations, but also depends on the type of washing agents. Previous studies indicated that CN has the characteristic bioactive constituents of sesquiterpene lactones such as coriamyrtin, tutin, and hydroxycoriatin

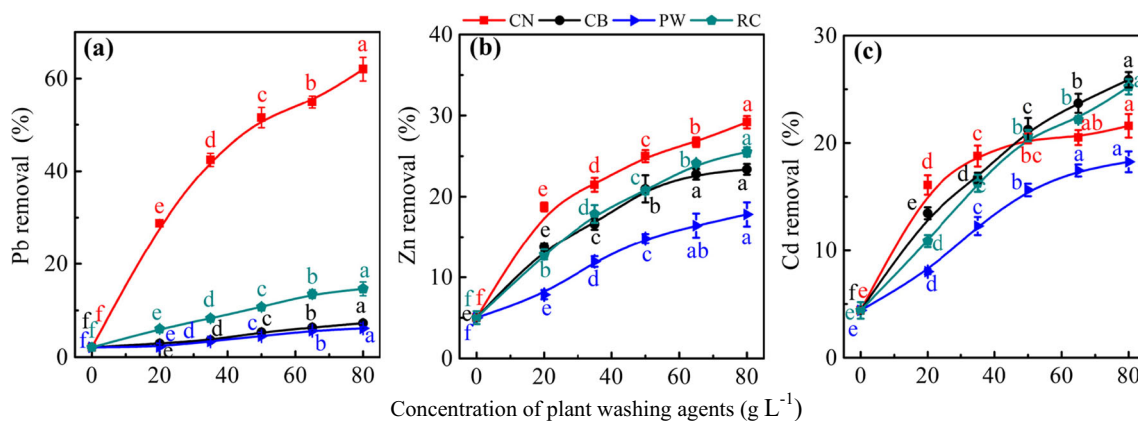


Fig. 1 Effect of the concentrations on the removal of Pb (a), Zn (b), and Cd (c) with plant washing agents from soil. CN *Coriaria nepalensis*, CB *Clematis brevicaudata*, PW *Pistacia weinmannifolia*, RC *Ricinus*

communis. Different letters in the same line indicate significant difference ($p < 0.05$)

(Yang et al. 2011; Zhao et al. 2012), and these components may be resulted in that the metal removal efficiencies by CN were higher than those of others. CB has triterpenoid saponins (Hao et al. 2013), *n*-hexadecanoic acid, and (*Z, Z*)-9,12-octadecadienoic acid (Zeng et al. 2007), and RC contains ricinoleic acid, linoleic acid, stearic acid, and sitosterol (Tyagi et al. 2013). Additionally, phytochemical studies revealed that PW is rich in gallotannins and related phenolic compounds (Zhao et al. 2005). Thus, the different components of plants might lead to the different washing efficiencies via the strength of their interactions with soil metals during chelating or ion exchange reactions.

Effect of pH on the removal of soil Pb, Zn, and Cd

The pH is an important factor for the washing efficiency by affecting the metal adsorption and desorption from soil colloids (Zou et al. 2009). As shown in Fig. 2, the washing efficiencies of soil Pb, Zn, and Cd by the four agents decreased with increasing solution pH. As the pH from 3.0 to 6.0, their

removal efficiencies by the agents sharply decreased ($p < 0.05$). This trend was similar to the washing of Pb by low molecular weight organic acid combined with nanoscale zero-valent iron (Wang et al. 2014). At pH 3.0, four plant washing agents for the removal of soil Pb, Zn, and Cd were relatively high. Under acidic conditions, the metal ions were easily desorbed from soil colloids for the solubility of carbonate-bound metals increased or exchanged with H^+ from the soil surface functional groups (Begum et al. 2012). As the pH beyond 6.0, the soil Pb, Zn, and Cd removal showed either a stable or an increasing trend (Fig. 2). At neutral or alkaline conditions, the lower removal abilities of heavy metals in soil might result from the low solubility of metal oxides or precipitate by the formation of metal hydroxyl complexes (Begum et al. 2013).

Effect of washing time on the removal of soil Pb, Zn, and Cd

Removal of heavy metals from contaminated soil is a dynamic equilibrium of adsorption and desorption process (Bradl 2004;

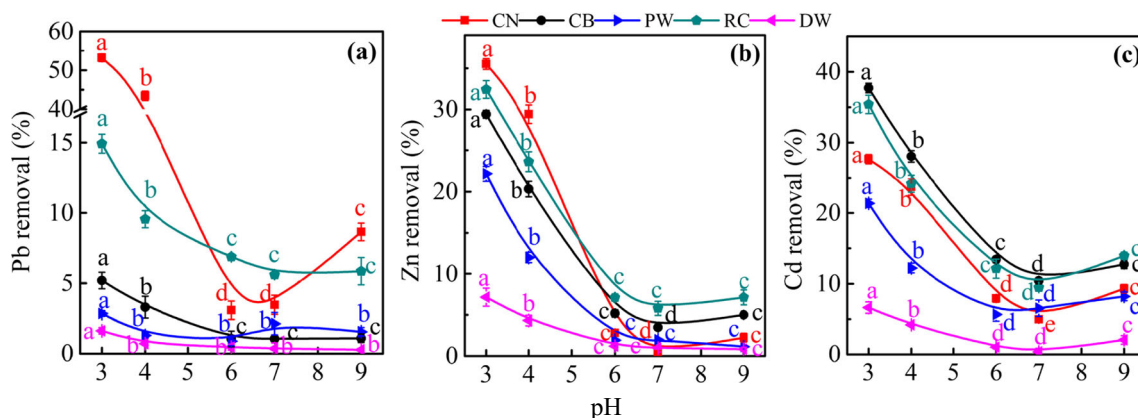


Fig. 2 Effect of the pH on the removal of Pb (a), Zn (b), and Cd (c) with plant washing agents from soil. CN *Coriaria nepalensis*, CB *Clematis brevicaudata*, PW *Pistacia weinmannifolia*, RC *Ricinus communis*, DW

distilled water. Different letters in the same line indicate significant difference ($p < 0.05$)

Sajadi Tabar and Jalali 2013), and the process needs to take some time. Thus, the washing time is another key parameter that influences the metal removal efficiency. In the current study, the effects of reaction time on soil Pb, Zn, and Cd removal were investigated at the concentrations of the reagents of 50 g L⁻¹ at pH 4.0. As shown in Fig. 3, soil Pb, Zn, and Cd removal efficiencies of the washing solutions presented different trends with increasing washing time. When the time was ≤1.5 h, CN for the metal removal efficiencies significantly increased with increasing washing time (*p* < 0.05). When the time was >1.5 h, the efficiencies were close to equilibrium and remained almost constant (*p* > 0.05). These change trends of Pb, Zn, and Cd removal by CN with reaction durations were similar to the experiments of the combination of EDTA and dithionite on the Pb and Zn removal at various periods (Kim et al. 2016). Currently, some researchers have pointed out that chemical reagents for the removal of soil heavy metals with time variation could be divided into two processes: the first process washed quickly, and the second process washed slowly (Bermond and Ghestem 2001). However, the trends of CB, PW, and RC for the removal of Pb were close to equilibrium and the removal of Zn increased gradually with the washing time from 0.5 to 4.0 h, while the trends of Cd removal efficiencies by them were different with increasing reaction time. These results may be ascribed to the complicated components among different plants.

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) analysis is important to identify some characteristic functional groups, especially those groups in binding of metal ions (Farooq et al. 2010; Kostić et al. 2014). The obtained spectra of all plant agents before and after washing were measured by an FTIR spectrometer (Fig. 4, Table 1). Based on the assignment of peaks in Table 1, the four agents contain many functional groups such as -COOH, -OH, -NH₂, C-O-C, and C-O-P.

These functional groups appeared in the phytochemical components, such as coriamyrtin, hydroxycoriatin, *n*-hexadecanoic acid, ricinoleic acid, or related phenolic, and have been identified as potential sites to be responsible for binding metallic ions to the biomass (Chakravarty et al. 2010).

Comparing the spectral changes of each agent before and after washing, the FTIR peaks might shift in position, change in intensity, and increase or decrease in number, indicating that there existed interaction between the functional groups of plant agents and metal ions in soil colloid (Fig. 4). The first change was the typical and intense shift of bands in the agents, which were shifted to another bands at 3388–3410 and 1595–1626 cm⁻¹ for the increasing bond strength of hydroxyl and carboxyl groups during the soil washing process (Gutha et al. 2015), respectively. The second change was the disappeared peaks at 1431 cm⁻¹ in CN, 1403 cm⁻¹ in CB, 1693 and 1037 cm⁻¹ in PW, and 1415 cm⁻¹ in RC, indicating that hydroxyl and carboxyl groups participated in the soil washing process by ion exchange or complexation. The final change was new peaks at 1384 cm⁻¹ in CN, 1384 and 1045 cm⁻¹ in CB, and 1280 cm⁻¹ in RC after soil washing. These results might be ascribed by acidic solution, and H⁺ ions as donors in solution could be bound to the sites on the surface of organic molecule structure of CN, CB, and RC and form functional groups (-COOH, -NH₂, and -OH) (Chen et al. 2010). Besides, the intensities of these new peaks were in the order of CN > CB > RC, indicating that CN had more functional groups and led to the highest removal efficiencies for the removal of soil heavy metals. Therefore, FTIR analysis demonstrated that the ability of plant washing agents to remove heavy metals may result from bioactive substances with specific functional groups such as -COOH, -NH₂, and -OH.

Effect of washing on soil metal fractions

The fractions of metals within the soil solid matrix could explain the different removal efficiencies for various metals

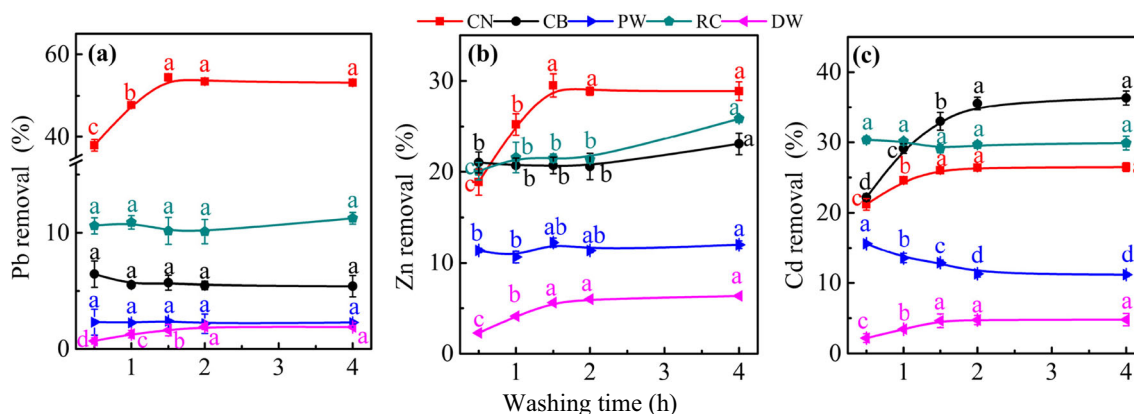


Fig. 3 Effect of the washing time on the removal of Pb (a), Zn (b), and Cd (c) with plant washing agents from soil. CN *Coriaria nepalensis*, CB *Clematis brevicaudata*, PW *Pistacia weinmannifolia*, RC *Ricinus*

communis, DW distilled water. Different letters in the same line indicate significant difference (*p* < 0.05)

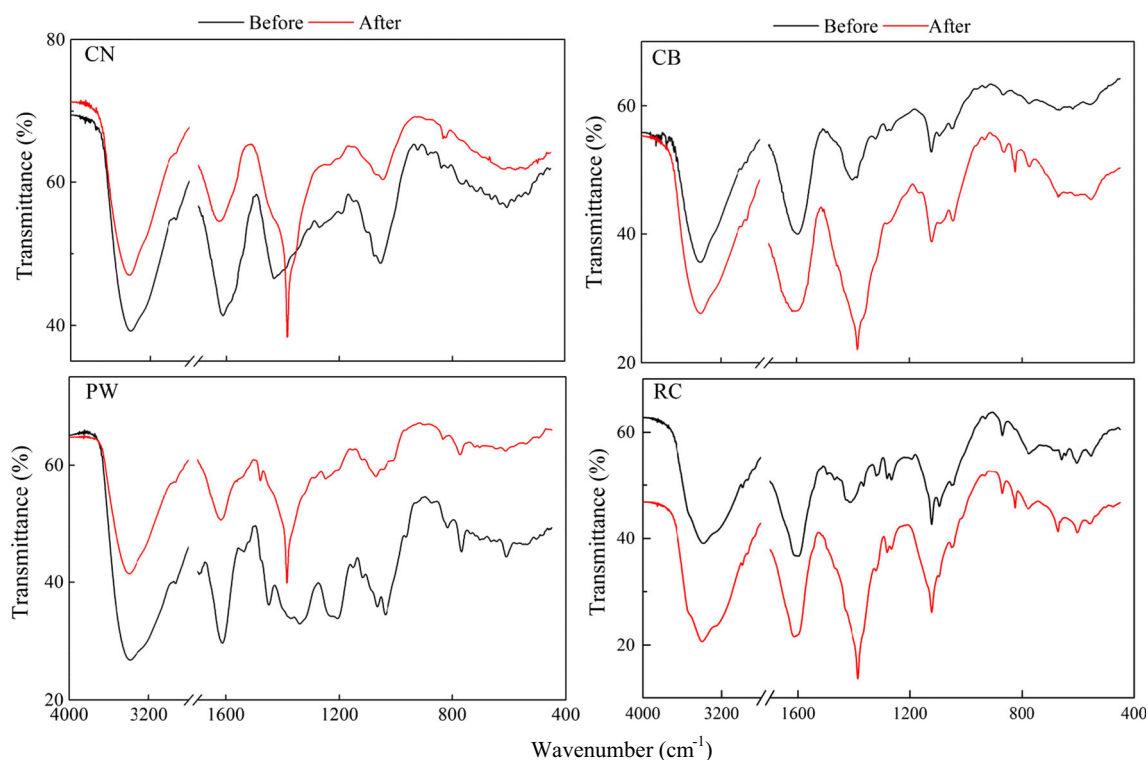


Fig. 4 FTIR spectra of four plant washing agents before and after washing at pH 4.0. *CN* *Coriaria nepalensis*, *CB* *Clematis brevicaudata*, *PW* *Pistacia weinmannifolia*, *RC* *Ricinus communis*

(Barona et al. 2001). The mobility and distribution of Pb, Zn, and Cd fractions in soils before and after washing with four plant washing agents at pH 4.0 were determined by the BCR sequential extraction procedure. The results revealed that 90.93, 80.04, and 89.23% of the total Pb, Zn, and Cd contents in the contaminated soil were bound in the non-detrital

fractions. The non-detrital fraction represents the metal amounts partitioned cumulatively in the exchangeable, reducible, and oxidizable fractions other than those associated with the residual fraction and could be removed easily by washing (Begum et al. 2013). As shown in Fig. 5, a significant proportion of the Pb (59.11%) was partitioned in the reducible

Table 1 Wave number of infrared adsorption peaks of four plant washing agents before and after washing at pH 4.0

Wave number (cm ⁻¹)		Groups		Reference					
CN	CB	PW	RC						
Before	After	Before	After	Before	After				
3399	3410	3401	3408	3389	3399	3388	3399	-OH stretching	Chen et al. (2010); Wang et al. (2015)
-	-	-	-	1693	-	-	-	Hydroxyl (-OH) deformation vibration of carboxylic group	Calero et al. (2013)
1613	1626	1595	1616	1611	1617	1598	1611	Asymmetric stretching of the carboxylic C=O double bond	Wang et al. (2015); Calero et al. (2013); Barka et al. (2013)
1431	-	1403	-	1448	1478	1415	-	Phenolic O-H and C=O stretching of carboxylates	Calero et al. (2013); Barka et al. (2013)
-	1384	-	1384	1339	1384	1318	1384	N-H groups	Li et al. (2009)
-	-	-	-	1206	1248	-	1280	C=O bond of non-ionic carboxylic acids (-COOH)	Farooq et al. (2010)
1045	1044	1122	1121	1066	1071	1122	1122	C-O-C, C-O-P, and O-H of polysaccharides	Li et al. (2008); Chakravarty et al. (2010)
-	-	-	1045	1037	-	-	-	C-O-C, C-O-P, and O-H of polysaccharides	Li et al. (2008); Chakravarty et al. (2010)

CN *Coriaria nepalensis*, *CB* *Clematis brevicaudata*, *PW* *Pistacia weinmannifolia*, *RC* *Ricinus communis*

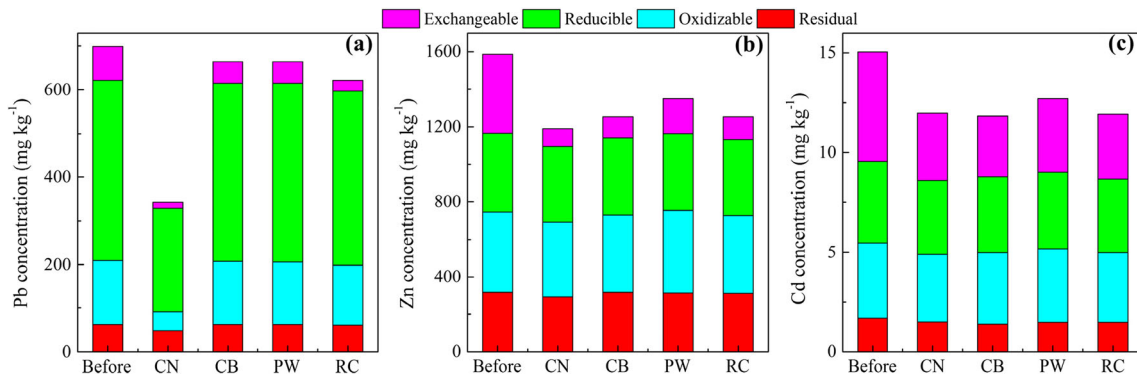


Fig. 5 Comparative distribution of Pb (a), Zn (b), and Cd (c) in the solid phase before and after soil washing at pH 4.0 with four plant washing agents. CN *Coriaria nepalensis*, CB *Clematis brevicaudata*, PW *Pistacia weinmannifolia*, RC *Ricinus communis*

fraction, while the Zn and Cd were equivalently distributed in all fractions approximately. The metal contents of exchangeable fraction for soil Pb, Zn, and Cd were reduced by 10.24–20.51% after washing with the four washing agents except for Pb with CB and PW (about 4%). The reductions of reducible, oxidizable, and residual fractions of heavy metals washed with CN were higher than those of the other three washing agents except for residual fraction of Cd. To the contrary, the reduction of residual fraction for Cd washed by CN was lower than that of the other three agents. The oxidizable fraction represents the metal ions bound to the organic matter, humic acids, and sulfides, which is the less labile forms, while the residual fraction, which is incorporated into the crystalline lattice of the soil minerals, is unlikely to be extracted easily (Pueyo et al. 2008; Tandy et al. 2004). The various removal rates among different fractions in soils may be attributed to the different functional groups in the four agents.

Conclusions

This study investigated four plant materials—CN, CB, PW, and RC—as eco-friendly plant washing agents to remove Pb, Zn, and Cd from contaminated soil. The concentrations of the agents, pH, and reaction time significantly affected the Pb, Zn, and Cd removal ($p < 0.05$). The removal efficiencies increased in response to the increasing concentrations of the agents, decreased with the increasing pH, and presented different trends with the time increasing. Results showed that four plant washing agents could be used for removing soil heavy metals, and CN was the best washing agent among the four reagents generally. The highest Pb, Zn, and Cd removal efficiencies by CN were 62.02, 29.18, and 21.60% at the concentrations of 80 g L^{-1} , respectively. Therefore, these plant materials could be potential eco-friendly plant washing agents to remove soil heavy metals, because they contain many functional groups such as $-\text{OH}$, $-\text{NH}_2$, and $-\text{COOH}$ and may react with heavy metal ions by ion exchange, complexation, and chemical reactions with surface sites. Hence, the various removal

efficiencies for heavy metals by the reagents may be in accordance with the functional groups on different plant chemical compositions and the types of metals.

Although the plant washing agents have demonstrated to be efficient in removing heavy metals, their washing mechanisms for the removal of soil metals were required for further study.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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