



Optimizing extraction procedures for better removal of potentially toxic elements during EDTA-assisted soil washing

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Abstract

Purpose Ethylenediaminetetraacetic acid (EDTA)-enhanced soil washing is an important technique of removing potentially toxic elements (PTEs) from contaminated soils. Conventional mechanical shaking (CMS) method is widely adopted in soil washing. However, it consumes a considerable amount of time and energy. Extraction methods which need less contact time or power, such as static equilibrium extraction (SEE) and ultrasound-assisted extraction (UAE), are potential to replace CMS in industrial application.

Methods The washing process of the soil from a contaminated site was optimized by investigating various extraction conditions, including EDTA concentration, contact time, and different extraction methods, such as CMS, SEE, and UAE, in this study.

Results The results indicated that EDTA greatly enhanced the removal of cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) from the soil. The EDTA was more effective in removing Pb and Cu than Cd and Zn, regardless of the extraction method. This might be mainly attributed to the strong complexation capacity of EDTA with Pb and Cu and geochemical distribution of the target PTEs. The three extraction methods were almost equally efficient, while SEE required less energy and UAE needed shortened contact time compared with CMS.

Conclusion Based on the above results, SEE and UAE are promising alternatives to CMS for cleaning up PTEs-contaminated soils.

Keywords Static equilibrium extraction · Ultrasound-assisted extraction · Soil washing · Heavy metal · Chelant

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1 Introduction

The potentially toxic elements (PTEs) have adverse effects on the soil ecosystem and human health because they are highly persistent in the environment and can easily enter the human food chain (Bandara et al. 2020; Rinklebe et al. 2020; Zhai et al. 2018). A nationwide soil investigation in China showed that 16.1% of collected soil samples were contaminated according to its standards, and 82.8% of the exceedances were caused by PTEs (Zhao et al. 2015). The high content of PTEs in soils might be attributed to a variety of anthropogenic activities, e.g., land application of wastes, irrigation with wastewater, emission from mining, smelting and other industrial activities, and application of pesticides and chemical fertilizers (Bandara et al. 2020; Beiyuan et al. 2017a; Liu et al. 2019a). Therefore, the development of remediation methods for the PTEs-contaminated soil has become an urgent task for both protecting the soil ecosystem and public health (Mao et al. 2018).

Many available technologies have been developed to restore the soils contaminated with PTEs, using physical, chemical, electrokinetic, and biological methods (e.g., Beiyuan et al. 2020; Bolan et al. 2014; Chen et al. 2020; Han et al. 2019; Li et al. 2020; Liu et al. 2018; Wang et al. 2020; Wu et al. 2019; Xia et al. 2019). Among the technologies, soil washing, which can mobilize PTEs then extract them from soils, is considered one of the most effective *ex situ* remediation technologies (Klik et al. 2020). A range of extractants has been used to extract PTEs from soils, for example, various inorganic acids and salts (e.g., HNO_3 , H_2SO_4 , and NH_4Cl) (Meng et al. 2016; Yoo et al. 2018), organic acids (e.g., citric acid, oxalic acid, and tartaric acid) (Beiyuan et al. 2017b; Meng et al. 2017; Tsang and Hartley 2014), strong chelants (e.g., ethylenediaminetetraacetic acid (EDTA) and [S,S]-ethylene-diamine-disuccinic-acid (EDDS)) (Beiyuan et al. 2018a, b; Zupanc et al. 2014) and surfactants (e.g., saponin) (Gusiatin and Klimiuk 2012). The removal efficiencies of PTEs can be varied, depending on the capacity of chelants, the properties of PTEs in the soils, and the soil properties.

The EDTA, one of the typical chelants, is an excellent reagent for removal of PTEs from contaminated soils (Hasegawa et al. 2019; Meng et al. 2016) due to (1) its strong chelating capacity with PTEs (especially for Cd, Cu, Pb, and Zn), (2) treatability for a broad range of soil types, and (3) reusability (Lestan et al. 2008). Generally, the primary mechanism for chelants to extract metals from soil is considered to be a desorption-complexation-dissolution process. The EDTA can quickly and directly break down some weak bonds between PTEs and soils, and the dissolution of the metal-EDTA complexes can indirectly destabilize the metal-oxygen bonds in the mineral (Beiyuan et al. 2018b; Tsang et al. 2007; Zhang et al. 2010). As a result, metal detachment happened from the surface of oxide and form soluble metal-EDTA complexes,

which keep the metals in solution (Begum et al. 2012). Some recent studies concerned about the limited biodegradability of EDTA and suggested to use biodegradable chelants, such as EDDS, N,N-bis(carboxymethyl)-L-glutamic acid (GLDA) and lignin-based poly(acrylic acid) to replace EDTA (Beiyuan et al. 2018a; Tsang and Hartley 2014; Zhao et al. 2019). However, its relatively low costs, strong complexation capacity to metals, and recyclability make EDTA still a prevalent choice for PTEs-extraction in contaminated soils.

Well soil dispersion, which can create efficient contact between the contaminated soil particles and extractant, is also a key factor affecting the extraction efficacy of contaminants, besides the selection of the extractant. Conventional mechanical shaking (CMS) is a typical method to disperse the soil particles, which can cause violent mixing and turbulence on a macro-scale, and contribute to more physical contact depending on the mixing intensity (Dermont et al. 2008; Son et al. 2011). As a result, PTEs that are weakly associated with the surface of soil particles can be easily removed with the help of mechanical shaking (Dermont et al. 2008). However, CMS needs extra electric energy input and takes a long time, which might cause a higher expense.

Static equilibrium extraction (SEE) requires no external force, thus it could become an economically attractive alternative if it can reach similar extraction efficiencies of PTEs as the conventional shaking method. Another attractive dispersion method is the ultrasound-assisted extraction (UAE), which only needs a short reaction time of 15–60 min (Wang et al. 2015). The ultrasonic extraction technique has been widely used for the treatment of contaminated soils because the presence of ultrasound can enhance the removal efficiency of PTEs. This method involves the use of ultrasound waves to accelerate extraction because the ultrasound waves are able to disrupt particles by aggressively agitating solutions. Intimate mixing and powerful physical and chemical reactions are achieved by applying intense and high-frequency sound to liquids or slurries (Hwang et al. 2007). Such particle disruption exposes fresh surfaces that therefore enable an extraction agent to penetrate particles (De La Calle et al. 2013; Hwang et al. 2007). The most widely accepted mechanism for ultrasound-assisted extraction is based on the implosion of cavitation bubbles produced by ultrasonication of liquid in the vicinity of a solid surface. The ultrasound-assisted extraction procedure can generate intense local high temperatures and pressures, reaching up to 5500 °C and 50 MPa. These localized temperatures and pressures result in high-velocity inter-particle collisions that can contribute to particle size reduction and thus, improve extraction (Hashemi et al. 2012; Pham et al. 2013; Picó 2013).

Many studies have been conducted to optimize extraction conditions and procedures using CMS with different extraction agents. Little is known, however, about the use of SEE as an extraction procedure for heavy metals from soil. So far, the

UAE procedure has been successfully applied to enhance the extraction of heavy metals, aliphatic and polycyclic aromatic hydrocarbons, and organic chlorine pesticides from various environmental matrices, such as soil, sewage sludge, water, and sediments (Chen et al. 2016; de La Rochebrochard et al. 2013; Santos et al. 2016). However, information is limited on the ultrasonic extraction of the PTEs from soils. Therefore, the aims of this paper are to (1) optimize removal efficiencies of four PTEs (Cd, Cu, Pb, and Zn) from soil by washing with EDTA using three different extraction procedures (CMS, SEE, and UAE) under various concentrations of EDTA, contact times, and ultrasonic power, and (2) compare the optimized removal efficiencies of PTEs for the three extraction procedures in order to determine the best conditions for remediating PTEs-contaminated soils.

2 Material and methods

2.1 Soil sampling

Surface soil (0–20 cm) was sampled from a contaminated site located near a copper smelter factory, in Fuyang, Hangzhou City, Zhejiang Province, China. Nine sub-samples of soil were randomly collected on site and well mixed to make a representative sample. The collected soils were air-dried, ground, and passed through a 2-mm plastic sieve. The homogenized soil samples were stored in plastic containers prior to use.

2.2 Analytical procedures

2.2.1 Soil physiochemical properties

Soil pH was measured in deionized water at a soil-to-liquid ratio of 1:2.5 (w/v). Soil organic matter (SOM) was determined by the Walkley-Black method (Walkley 1935; Xu et al. 2017). Soil particle size was analyzed using the hydrometer method (Lu 1999). The total contents of PTEs in the soil were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 2000, PerkinElmer Co., USA) after acid digestion with an acidic mixture of HF-HNO₃-HClO₄ (Lu 1999). The soil consisted of 47.7% of sand, 36.0% of silt, and 16.3% of clay. It contained 19.9 g kg⁻¹ of organic matter with a pH value of 8.2. It was contaminated by Cd, Cu, Pb, and Zn, with total concentrations of 13.3, 740, 426, and 2134, respectively.

2.2.2 Geochemical distribution of PTEs

The geochemical distribution of Cd, Cu, Pb, and Zn in the contaminated soil (Fig. 1) was assessed by sequential extraction according to Tessier's method (Liu et al. 2019b; Tessier

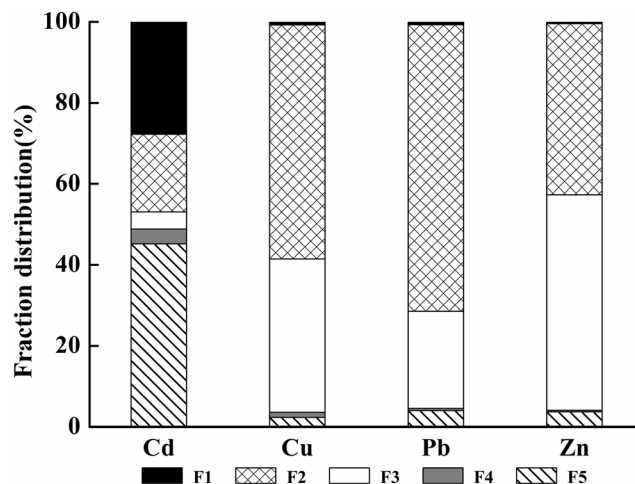


Fig. 1 Geochemical distribution of Cd, Cu, Pb, and Zn in the contaminated soils. F1, exchangeable fraction; F2, carbonate bound fraction; F3, Fe-Mn oxides bound fraction; F4, organic matter bound fraction; F5, residual fraction

et al. 1979). The detailed extraction conditions are presented in Table 1.

2.3 Batch experiment

All batch experiments were conducted in acid-rinsed 100-mL plastic centrifuge tubes. The EDTA (used as the Na₂-EDTA salt, analytical grade) was dissolved in ultrapure Milli-Q water for the preparation of all solutions. Tubes containing 1 g of contaminated soil at a liquid:soil ratio of 25:1 (v/w) were prepared for each extraction followed by addition of EDTA solution.

2.3.1 Conventional mechanical shaking

In order to determine the extraction efficiency of PTEs, solutions in seven different EDTA concentrations (0.005, 0.01, 0.03, 0.05, 0.07, 0.15, and 0.3 mol L⁻¹ which represent chelant-to-metal ratios of 2.7, 5.4, 16.2, 27.0, 37.8, 80.9, and 161.8, respectively) were used. The soil-EDTA slurries were mixed at room temperature using an end-over-end shaker at 180 rpm for 4 h. Furthermore, to examine the effect of contact time which also plays an important role in chemical extraction, a 0.03 mol L⁻¹ EDTA solution was shaken for 0.5, 4, 8, 12, 16, and 24 h.

2.3.2 Static equilibrium extractions

Same as CMS, EDTA solutions were prepared in seven different concentrations (0.005, 0.01, 0.03, 0.05, 0.07, 0.15, and 0.3 mol L⁻¹, which represent chelant-to-metal ratios of 2.7, 5.4, 16.2, 27.0, 37.8, 80.9, and 161.8, respectively). The EDTA solution was added into soil samples then kept still for 24 h at room temperature for the SEE method. In addition,

Table 1 Sequential extraction procedure for geochemical distribution of potentially toxic elements

Extraction step	Fraction	Extraction agents	Extraction conditions
1	Exchangeable	1 mol L ⁻¹ MgCl ₂ , pH 7	1 h, room temperature
2	Bound to carbonates	1 mol L ⁻¹ CH ₃ COONa, pH 5	5 h, room temperature
3	Bound to Fe-Mn oxides	0.04 mol L ⁻¹ NH ₂ OH-HCl in 25% (v/v) CH ₃ COOH	6 h, 96 °C
4	Bound to organic matter	30% H ₂ O ₂ + HNO ₃ (pH 2), 3.2 mol L ⁻¹ CH ₃ COONH ₄ in 20% (v/v) HNO ₃	5 h, 85 °C
5	Residual	Concentrated HCl, HF, HClO ₄ , HNO ₃	6 h, 190 °C

the removal efficiencies of the PTEs were evaluated for different contact time: 0.5, 4, 8, 16, and 24 h, at a constant concentration of 0.07 mol L⁻¹.

2.3.3 Ultrasound-assisted extractions

A 700 W, 40 kHz high-intensity ultrasonic apparatus was used for ultrasound-assisted extraction. Similarly, seven different concentrations of EDTA solution (0.005, 0.01, 0.03, 0.05, 0.07, 0.15, and 0.3 mol L⁻¹, which represent chelant-to-metal ratios of 2.7, 5.4, 16.2, 27.0, 37.8, 80.9, and 161.8, respectively) were prepared and sonicated for 30 min at an ultrasonic power of 500 W. In addition, three different contact times (5, 15, and 30 min) were tested using 500 W of power at a concentration of 0.03 mol L⁻¹ EDTA. The effect of ultrasonic power was also studied at three levels (200, 350, and 500 W) at a concentration of 0.03 mol L⁻¹ EDTA and a contact time of 30 min.

All the slurry samples of the above different extraction procedures were centrifuged at 4000 rpm for 10 min. The supernatants of the samples were filtered, acidified with 5% HNO₃, and stored at 4 °C prior to ICP analysis. All tests were performed in triplicate, and the results are presented as the average of three extracts.

3 Results

3.1 Extraction efficiencies of PTEs by conventional mechanical shaking

The removal efficiencies of Cu, Pb, and Zn increased with increasing EDTA concentrations up to EDTA concentration of 0.01 mol L⁻¹ by CMS (Fig. 2a). The removal of Pb was at an optimum when extracted with EDTA concentrations between 0.01 and 0.07 mol L⁻¹. The extraction efficiencies for Cu, Pb, and Zn were decreased when the EDTA concentration was higher than 0.07 mol L⁻¹. The removal efficiency of Cd did not change with the increasing EDTA concentrations, which was kept in around 60%.

Among the four targeted PTEs, Pb showed the highest removal efficiency with 0.03 mol L⁻¹ EDTA (Fig. 2b). An

increasing contact time resulted in a corresponding increase in the quantity of Cd, Cu, and Pb extracted until the removal efficiency leveled off. The removal efficiency of Zn considerably increased over the first 4 h, followed by a gradual increase in total removal efficiency over the following hours (8, 12, 16, and 24 h).

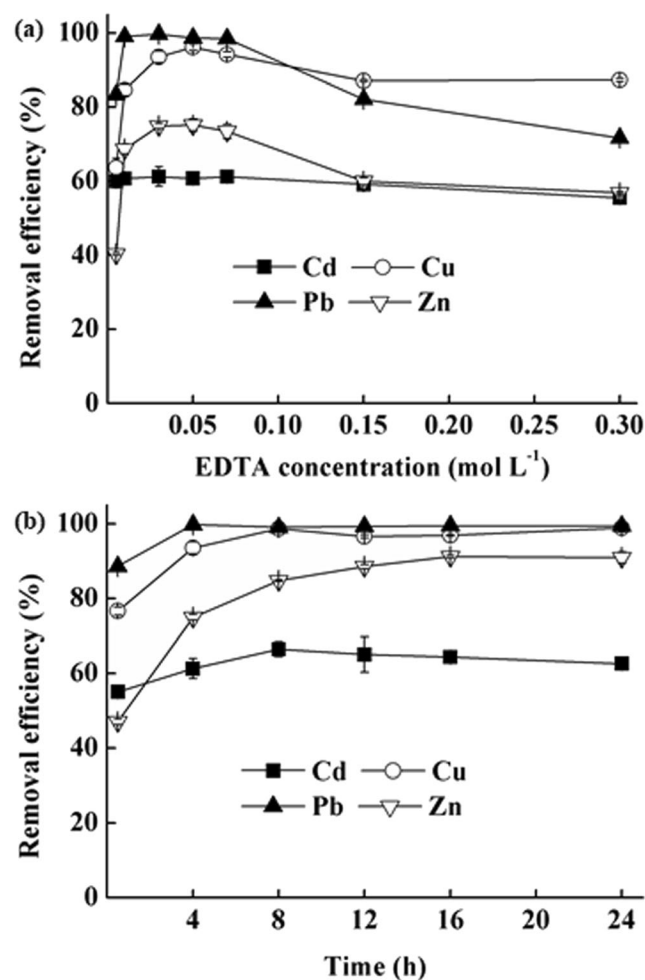


Fig. 2 Removal efficiencies of Cd, Cu, Pb, and Zn **a** under different concentrations of EDTA (at a liquid:soil ratio of 25:1 and contact time of 4 h) and **b** under different contact time (at a liquid:soil ratio of 25:1 and EDTA concentration of 0.03 mol L⁻¹) using the conventional mechanical shaking extraction method. Error bars represent the standard deviation of three replicates

3.2 Extraction efficiencies of PTEs by static equilibrium extraction

The removal efficiency of Cd, Cu, Pb, and Zn increased with increasing concentration of EDTA and then decreased at a concentration of 0.07 mol L⁻¹ by SEE (Fig. 3a). By increasing the EDTA concentration from 0.005 mol L⁻¹ to 0.07 mol L⁻¹, the removal efficiencies of Cu, Pb, and Zn increased considerably (from 42.5 to 94.8%, 58.4 to 99.4%, and 23.3 to 77.8%, respectively). The removal efficiency of Cd only increased a limited amount (from 53.3 to 60.4%) in response to an increase in EDTA concentration. When the concentrations were greater than 0.07 mol L⁻¹, removal efficiencies decreased for all four metals.

Increasing the contact time from 0.5 h to 24 h resulted in greater removal efficiencies for Cu, Pb, Zn, and Cd (Fig. 3b). The increment of EDTA concentration was more obvious in

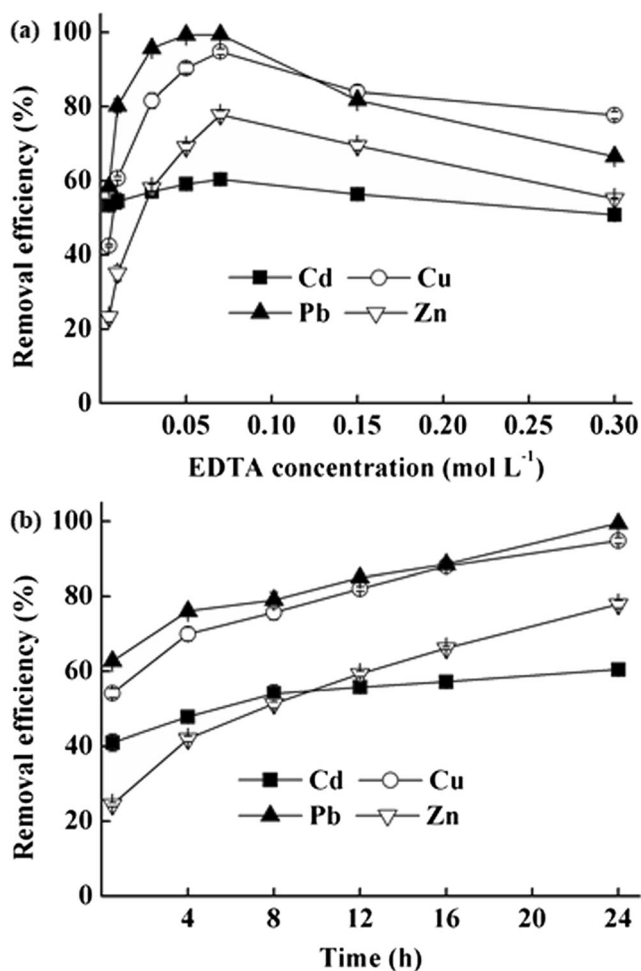


Fig. 3 Removal efficiencies of Cd, Cu, Pb, and Zn **a** under different concentrations of EDTA (at a liquid:soil ratio of 25:1 and contact time of 24 h) and **b** under different contact time (at a liquid:soil ratio of 25:1 and EDTA concentration of 0.07 mol L⁻¹) using the static equilibrium extraction method. Error bars represent the standard deviation of three replicates

the contact time from 0.5 h to 8 h compared to greater than 8 h, as was evident from the slopes of the curves in Fig. 3b.

3.3 Extraction efficiencies of PTEs by ultrasound-assisted extraction

The removal efficiency of Cd, Cu, Pb, and Zn increased when the EDTA concentration increased from 0.005 to 0.03 mol L⁻¹ by UAE (Fig. 4a). However, increasing the EDTA concentration from 0.03 to 0.30 mol L⁻¹ resulted in lower removal efficiencies for Cu, Pb, and Zn but not Cd. The Cd extraction efficiency was not significantly different when the EDTA concentration ranged between 0.03 and 0.30 mol L⁻¹. The removal efficiencies of the target PTEs were in an order of Pb > Cu > Zn > Cd.

The removal efficiency of tested heavy metals gradually increased with the increasing sonication time period and

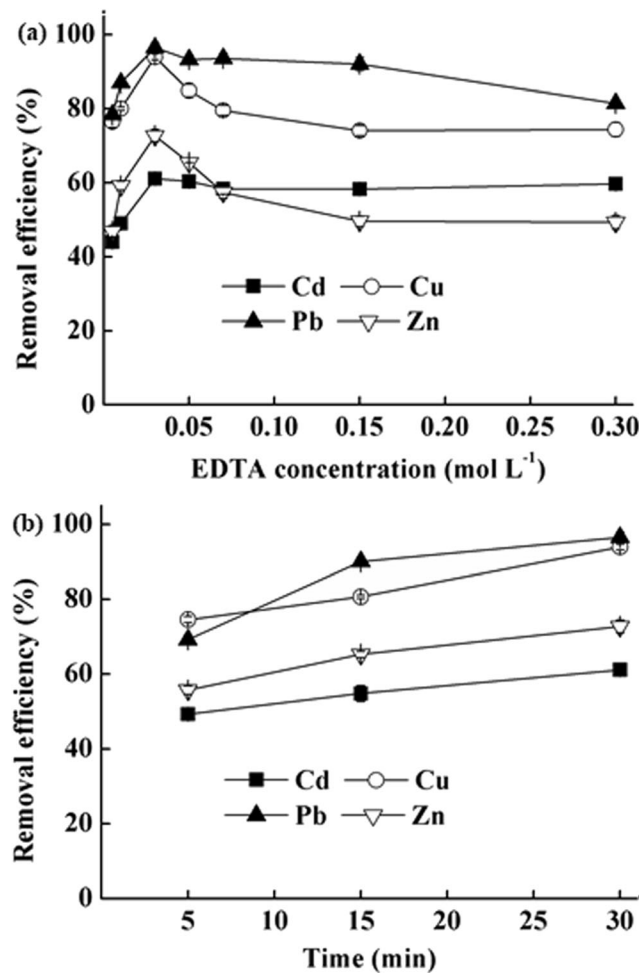


Fig. 4 Removal efficiencies of Cd, Cu, Pb, and Zn **a** under different concentrations of EDTA (at a liquid:soil ratio of 25:1, contact time of 30 min, sonication power of 500 W) and **b** under different sonication time (at a liquid:soil ratio of 25:1, EDTA concentration of 0.03 mol L⁻¹, sonication power of 500 W) using the ultrasound-assisted extraction method. Error bars represent the standard deviation of three replicates

ultrasonic power (Figs. 4b and 5). The optimum results were achieved after 30 min at a sonication power of 500 W.

4 Discussion

4.1 Extraction efficiencies of PTEs by EDTA

The removal efficiencies of Pb and Cu were higher than Cd and Zn, regardless of extraction approaches (Figs. 2, 3 and 4). This could be partly attributed to the slightly higher stability constants of Pb- and Cu-EDTA complexes compared to Cd and Zn. It has been well studied that the extraction capacity of EDTA is directly dependent on its ability to form stable complexes with PTEs (Li et al. 2012). The stability constants (log K) of the metal-EDTA complexes followed the order: Cu (18.8) \approx Pb (18.2) > Cd (16.5) \approx Zn (16.2) (Begum et al. 2012; Labanowski et al. 2008). The higher removal efficiencies of Pb and Cu might also be a result of that over 60% of them were bounded to the exchangeable and carbonates fractions (Fig. 1). The PTEs bounded to these fractions can be easily removed by chelants (Beiyuan et al. 2017b; Zhang et al. 2010). Other crucial reasons include initial content of PTEs in soils, competitions with cations (from co-contaminants or minerals), soil properties, reaction time, washing patterns, and conditions of EDTA (e.g., concentration, soil-to-solution ratio, and pH) (Beiyuan et al. 2018b). For example, Zupanc et al. (2014) found that EDTA extracted more Cd than Cu and Zn.

However, in the current study, Cd was the most difficult metal to be removed while nearly all the soil Pb was removed. This could be mainly contributed to speciation of Cd. The results of geochemical distribution showed that around

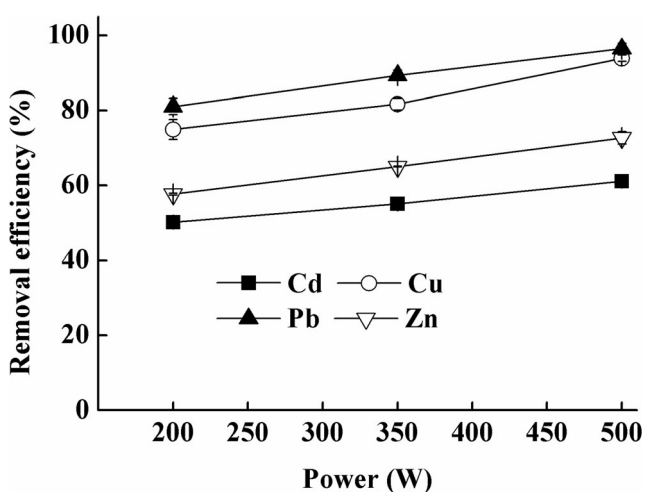


Fig. 5 Removal efficiencies of Cd, Cu, Pb, and Zn under different ultrasound power (at a liquid:soil ratio of 25:1, EDTA concentration of 0.03 mol L⁻¹, contact time of 30 min) using the ultrasound-assisted extraction method. Error bars represent the standard deviation of three replicates

45.2% of Cd bound to residual fraction (Fig. 1), which is difficult to be extracted by chelants (Matong et al. 2016). In addition, around 10% of Cd bound to organic matter and Fe/Mn oxides which are also difficult to be extracted by EDTA compared to Cd in exchangeable fraction and carbonate bound fraction. The solubility of carbonates can be greatly promoted in the presence of chelants, while the PTEs bound to Fe/Mn oxides can be disassociated by EDTA. The disassociation of Fe/Mn oxides can be affected by the crystalline form of Fe/Mn oxides and the condition of the system, such as pH and reaction time (Nowack and Sigg 1997). For example, the well-crystalline goethite can be dissolved much slower than amorphous iron oxides by EDTA and metal-EDTA complexes. These can further explain that the extraction of Zn was low compared to Pb and Cu in this study.

4.2 Effect of EDTA concentration

The concentration of chelants of soil washing affects the equilibrium speciation in such complex (Hasegawa et al. 2019). For the SEE and UAE, the removal efficiencies of the four PTEs increased with increasing EDTA concentration and reached a peak at a concentration of 0.07 and 0.03 mol L⁻¹, respectively (Figs. 3b and 4b). For the CMS extraction, the maximum removal efficiencies of Cu, Pb, and Zn reached at concentrations of 0.05, 0.01, and 0.03 mol L⁻¹, respectively (Fig. 2a). The CMS extraction was expected to minimize the consumption of EDTA. However, increasing the EDTA concentration further from 0.03 to 0.05 mol L⁻¹, only resulted in a small additional increase in the removal efficiency of Cu. Overall, the optimal concentrations for the CMS, SEE, and UAE were 0.03, 0.07, and 0.03 mol L⁻¹, respectively. Particularly, unlike the Cu, Pb, and Zn, the removal of Cd was less dependent on the concentration of EDTA. The maximum extraction efficiency of Cd kept steady (~60%) for all extraction methods, despite using a much higher concentration of EDTA. As discussed in Section 4.1, EDTA preferentially extracts metals from the labile bound fractions (e.g., exchangeable fraction and carbonate bound fraction) (Andrade et al. 2007), while a large amount of Cd existed in residue fraction in this study (Fig. 1).

Interestingly, greater concentrations of EDTA resulted in lower removal efficiencies of Cu, Pb, and Zn, which was observed in all three extraction methods, especially for those treatments extracted with more than 0.07 mol L⁻¹ EDTA. This is probably because EDTA molecules are not only able to form complexes with the target toxic metals but also able to form stable metal-EDTA complexes with large amounts of mineral metals in soils (Tandy et al. 2004; Zhang et al. 2013), e.g., Ca, Mg, Al, and Fe. These mineral metals, in high content, can therefore compete with the target PTEs for binding sites of EDTA. In addition, the largely formed mineral metal-chelant complexes can exchange with the metal-

chelant complexes of Cu, Pb, and Zn, which might lead to the lower removal efficiencies of the target PTEs. A higher concentration of chelants can also lead to low efficiency when large amounts of them are in mineral metal-chelant complexes and uncomplexed forms as indicated by Visual MINTEQ modeling results (Beiyuan et al. 2018b). Previous studies also suggested that excess amounts of EDTA only marginally or unproportionally contribute to the improvement of metal removal efficiencies (Zou et al. 2009). In this study, the high EDTA concentration employed could cause a matrix effect of analyte solutions and lead to reduced metal concentrations in the samples, which then decreased extraction efficiencies of PTEs. Therefore, a proper chelant-to-metal ratio should be tested before applying EDTA-enhanced extraction on the field.

4.3 Effect of contact time and sonication power

In the CMS extraction, the removal efficiencies of Cu, Pb, and Cd remained almost constant when the shaking time was greater than 4 h (Fig. 2b). This phenomenon occurred because the EDTA extraction process takes more time than the exchange of adsorbed metals for hydronium ions. Additionally, this was attributable to the fact that the EDTA molecules are larger in comparison with the hydronium ions and thus, they enter into the soil matrix with more difficulty (Gheju et al. 2011). It was observed that longer extraction time can lead to higher Zn extraction efficiency in the CMS extraction. This might be due to the higher proportion of Zn bound to Fe/Mn oxides (Fig. 1). The dissociation of iron (hydro)oxides by EDTA includes quick adsorption (a few minutes) and a relatively slow dissolution (after 2 h) (Nowack et al. 2006). Whereas, in the SEE extraction, an increasing contact time resulted in a corresponding increase in the quantities of the four PTEs extracted.

It was therefore obvious that the highest removal efficiencies of all target PTEs were obtained at the longest testing time

(30 min) and highest power (500 W), which is consistent with other studies (De La Calle et al. 2013). The ultrasound can be delivered into the solution, the heating created by attrition led to a slow but constant increase in temperature with increasing sonication time, which contributed to a release of PTEs in soils (Park and Son 2017; Picó 2013). A higher power of the UAE can contribute to higher heating temperature and a better contact condition of soil particles and EDTA. For instance, the higher power of ultrasound might enhance the decomposition of soil particles, resulting in a higher surface area of the soil particles.

Consequently, the optimal conditions were suggested as follows: (1) a contact time of 4 h in CMS; (2) a contact time of 24 h in SEE; (3) a contact time of 30 min and a sonication power of 500 W in UAE.

4.4 Comparisons of extraction methods: CMS, SEE, and UAE

Son et al. (2012) reported that soil washing processes showed high removal efficiencies due to the macro-scale and micro-scale violent desorption actions not only for the pollutants on the surface of the soil particles but also for the pollutants sorbed in the pores of soil particles. In this study, three extraction methods were independently investigated for their optimal extraction conditions. The highest removal efficiencies for Cd, Cu, Pb, and Zn were obtained with a concentration of 0.03 mol L⁻¹ for the CMS and UAE, and 0.07 mol L⁻¹ for the SEE, respectively. The calculated residual contents of PTEs in soils are below the limitations of Soil Environmental Quality - Risk Control Standard for Soil Contamination of Development Land in China (GB36600-2018) for Type 1 land, after washing by the CMS, SEE, and UAE on the optimal operating conditions (Table 2). The SEE required longer contact time than the CMS and UAE under the optimal condition, yet the SEE did not require external force which is more economical for application. In addition, in terms of the removal

Table 2 Residual contents of PTEs in soil after washing by the CMS, SEE, and UAE under the optimal operating conditions

Treatments	Residual content in soil (mg kg ⁻¹)			
	Cd	Cu	Pb	Zn
CMS ^a	0.52	47.99	1.25	535.80
SEE ^b	0.53	38.61	2.57	472.81
UAE ^c	0.52	45.15	15.15	582.29
Limits for Type 1 land in GB36600-2018 ^d	20	2000	400	Not applicable

^a 0.03 mol L⁻¹ EDTA, at a liquid:soil ratio of 25:1, and contact time of 4 h

^b 0.07 mol L⁻¹ EDTA, at a liquid:soil ratio of 25:1, and contact time of 24 h

^c 0.03 mol L⁻¹ EDTA, at a liquid:soil ratio of 25:1, contact time of 30 min, and sonication power of 500 W

^d Soil Environmental Quality - Risk Control Standard for Soil Contamination of Development Land in China (GB36600-2018)

efficiencies of the four PTEs, there was no actual difference between the three extraction methods. However, the SEE was clearly better at removing Zn than the other two methods due to the promoted contact time for the dissolution of iron (hydro)oxides. Nevertheless, when the ultrasonic power was applied, 30 min was sufficient to reach the same removal efficiency compared to 4 h for the CMS and 24 h for the SEE extraction. This indicated that ultrasound improved the extraction of PTEs through greatly reducing the extraction time. Kovács et al. (2018) also reported that ultrasound can efficiently enhance the extraction speed. Many physical effects, such as micro-jet and micro-streaming, can be generated with the help of ultrasound, therefore, enhancing the removal of contaminants from soil particles. A recent study reported that the removal efficiencies of PTEs bound to residual fraction can be enhanced by UAE (Son et al. 2019), yet the enhancement is not obvious in our study. This might be due to HCl used in their study, which is a strong acid that can break down the residual fraction with the help of UAE.

The use of ultrasound was very effective for the removal of PTEs in soils. The energy consumption for the UAE extraction, however, is difficult to determine from laboratory-scale experiments. Some researchers have compiled the basic information for the design of large-scale sonoreactors for advanced oxidation processes (AOPs) in homogeneous systems (Gogate et al. 2011; Lim et al. 2014). Long-term and large-scale scientific studies should be performed, to demonstrate the energy requirements and the large-scale feasibility of removing PTEs in soil using the UAE method. Furthermore, technical and economically feasible ways to reclaim EDTA in soil washing process are needed. Otherwise, secondary pollution may be caused by EDTA if it is not recycled or destroyed in the washing process, since EDTA has a low biodegradability which makes it resistant to biological and chemical degradation (Tandy et al. 2004).

Overall, the SEE and UAE both have the potential to be an alternative method for extracting PTEs from the soil.

5 Conclusions

The performance of the CMS, SEE, and UAE was evaluated under various EDTA concentrations and contact times. In general, the removal efficiencies of Cu and Pb were higher than those of Cd and Zn for the three tested methods, which is mainly attributed to their geochemical distribution and strong complexation capacity with EDTA. These methods were particularly efficient for Pb removal of the soil.

Although the optimal concentration in the SEE was higher than that in the CMS and UAE, there was no actual difference among the three approaches in terms of removal efficiency. Nevertheless, the SEE requires no external force leading like the intensive mixing between the contaminated soil and

EDTA solution required for the CMS and UAE extraction methods and would therefore likely be more economical. The greatest advantage of the UAE extraction method was that the contact time was very short (with a reduction of 87.5%) due to the combined effects of mechanical mixing at macro-scale and sonophysical effects at micro-scale level. Therefore, both the SEE and UAE have potential as an application for extracting PTEs from contaminated soils.

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References

- Andrade M, Prasher S, Hendershot W (2007) Optimizing the molarity of a EDTA washing solution for saturated-soil remediation of trace metal contaminated soils. *Environ Pollut* 147:781–790
- Bandara T, Franks A, Xu J, Bolan N, Wang H, Tang C (2020) Chemical and biological immobilization mechanisms of potentially toxic elements in biochar-amended soils. *Crit Rev Environ Sci Technol* 50: 903–978
- Begum ZA, Rahman IM, Tate Y, Sawai H, Maki T, Hasegawa H (2012) Remediation of toxic metal contaminated soil by washing with biodegradable aminopolycarboxylate chelants. *Chemosphere* 87:1161–1170
- Beiyuan J, Li J, Tsang DCW, Wang L, Poon CS, Li XD, Fendorf S (2017a) Fate of arsenic before and after chemical-enhanced washing of an arsenic-containing soil in Hong Kong. *Sci Total Environ* 599–600:679–688
- Beiyuan J, Tsang DCW, Valix M, Zhang W, Yang X, Ok YS, Li XD (2017b) Selective dissolution followed by EDOS washing of an e-waste contaminated soil: extraction efficiency, fate of residual metals, and impact on soil environment. *Chemosphere* 166:489–496
- Beiyuan J, Lau AYT, Tsang DCW, Zhang W, Kao C-M, Baek K, Ok YS, Li X-D (2018a) Chelant-enhanced washing of CCA-contaminated soil: coupled with selective dissolution or soil stabilization. *Sci Total Environ* 612C:1463–1472
- Beiyuan J, Tsang DCW, Valix M, Baek K, Ok YS, Zhang W, Bolan NS, Rinklebe J, Li X-D (2018b) Combined application of EDOS and EDTA for removal of potentially toxic elements under multiple soil washing schemes. *Chemosphere* 205:178–187
- Beiyuan J, Awad YM, Beckers F, Wang J, Tsang DCW, Ok YS, Wang S-L, Wang H, Rinklebe J (2020) (Im)mobilization and speciation of lead under dynamic redox conditions in a contaminated soil amended with pine sawdust biochar. *Environ Int* 135:105376
- Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham MB, Schechel K (2014) Remediation of heavy metal(-loid)s contaminated soils—to mobilize or to immobilize? *J Hazard Mater* 266:141–166
- Chen F, Tan M, Ma J, Li G, Qu J (2016) Restoration of manufactured gas plant site soil through combined ultrasound-assisted soil washing and bioaugmentation. *Chemosphere* 146:289–299
- Chen H, Yang X, Wang H, Sarkar B, Shaheen SM, Gielen G, Bolan N, Guo J, Che L, Sun H, Rinklebe J (2020) Animal carcass- and wood-derived biochars improved nutrient bioavailability, enzyme activity, and plant growth in metal-phthalic acid ester co-contaminated soils: a trial for reclamation and improvement of degraded soils. *J Environ Manage* 261:110246

- De La Calle I, Cabaleiro N, Lavilla I, Bendicho C (2013) Ultrasound-assisted single extraction tests for rapid assessment of metal extractability from soils by total reflection X-ray fluorescence. *J Hazard Mater* 260:202–209
- de La Rochebrochard S, Naffrechoux E, Drogui P, Mercier G, Blais J-F (2013) Low frequency ultrasound-assisted leaching of sewage sludge for toxic metal removal, dewatering and fertilizing properties preservation. *Ultrason Sonochem* 20:109–117
- Dermont G, Bergeron M, Mercier G, Richer-Lafleche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. *J Hazard Mater* 152:1–31
- Gheju M, Pode R, Manea F (2011) Comparative heavy metal chemical extraction from anaerobically digested biosolids. *Hydrometallurgy* 108:115–121
- Gogate PR, Sutkar VS, Pandit AB (2011) Sonochemical reactors: important design and scale up considerations with a special emphasis on heterogeneous systems. *Chem Eng J* 166:1066–1082
- Gusiatin ZM, Klimiuk E (2012) Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin. *Chemosphere* 86:383–391
- Han R, Dai H, Zhan J, Wei S (2019) Clean extracts from accumulator efficiently improved *Solanum nigrum* L. accumulating Cd and Pb in soil. *J Clean Prod* 239:118055
- Hasegawa H, Mamun MAA, Tsukagoshi Y, Ishii K, Sawai H, Begum ZA, Asami MS, Maki T, Rahman IMM (2019) Chelator-assisted washing for the extraction of lead, copper, and zinc from contaminated soils: a remediation approach. *Appl Geochem* 109:104397
- Hashemi M, Jahanshahi N, Habibi A (2012) Application of ultrasound-assisted emulsification microextraction for determination of benzene, toluene, ethylbenzene and o-xylene in water samples by gas chromatography. *Desalination* 288:93–97
- Hwang S-S, Park J-S, Namkoong W (2007) Ultrasonic-assisted extraction to release heavy metals from contaminated soil. *J Ind Eng Chem* 13:650–656
- Klik B, Kulikowska D, Gusiatin ZM, Pasieczna-Patkowska S (2020) Washing agents from sewage sludge: efficiency of Cd removal from highly contaminated soils and effect on soil organic balance. *J Soil Sediment* 20:284–296
- Kovács K, Halász G, Takács A, Heltai G, Széles É, Györi Z, Horváth M (2018) Study of ultrasound-assisted sequential extraction procedure for potentially toxic element content of soils and sediments. *Microchem J* 136:80–84
- Labanowski J, Monna F, Bermond A, Cambier P, Fernandez C, Lamy I, van Oort F (2008) Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate. *Environ Pollut* 152:693–701
- Lestan D, Luo CL, Li XD (2008) The use of chelating agents in the remediation of metal-contaminated soils: a review. *Environ Pollut* 153:3–13
- Li Y, Hu X, Song X, Sun T (2012) Remediation of cadmium-contaminated soil by extraction with para-sulphonatothiacalix[4]arene, a novel supramolecular receptor. *Environ Pollut* 167:93–100
- Li J, Wang S-L, Zhang J, Zheng L, Chen D, Wu Z, Shaheen SM, Rinklebe J, Ok YS, Wang H, Wu W (2020) Coconut-fiber biochar reduced the bioavailability of lead but increased its translocation rate in rice plants: elucidation of immobilization mechanisms and significance of iron plaque barrier on roots using spectroscopic techniques. *J Hazard Mater* 389:122117
- Lim M, Ashokkumar M, Son Y (2014) The effects of liquid height/volume, initial concentration of reactant and acoustic power on sonochemical oxidation. *Ultrason Sonochem* 21:1988–1993
- Liu L, Li W, Song W, Guo M (2018) Remediation techniques for heavy metal-contaminated soils: principles and applicability. *Sci Total Environ* 633:206–219
- Liu J, Luo X, Sun Y, Tsang DCW, Qi J, Zhang W, Li N, Yin M, Wang J, Lippold H, Chen Y, Sheng G (2019a) Thallium pollution in China and removal technologies for waters: a review. *Environ Int* 126:771–790
- Liu J, Ren S, Zhou Y, Tsang DCW, Lippold H, Wang J, Yin M, Xiao T, Luo X, Chen Y (2019b) High contamination risks of thallium and associated metal(loid)s in fluvial sediments from a steel-making area and implications for environmental management. *J Environ Manage* 250:109513
- Lu R (1999) Analytical methods of soil agrochemistry. China Agricultural Science and Technology Press, Beijing, pp 85–96
- Mao G, Shi T, Zhang S, Crittenden J, Guo S, Du H (2018) Bibliometric analysis of insights into soil remediation. *J Soil Sediment* 18:2520–2534
- Matong JM, Nyaba L, Nomngongo PN (2016) Fractionation of trace elements in agricultural soils using ultrasound assisted sequential extraction prior to inductively coupled plasma mass spectrometric determination. *Chemosphere* 154:249–257
- Meng W, Chen J, Wang X (2016) Removal of arsenic and cadmium with sequential soil washing techniques using Na₂ EDTA, oxalic and phosphoric acid: optimization conditions, removal effectiveness and ecological risks. *Chemosphere* 156:252–261
- Meng F, Yuan G, Wei J, Bi D, Ok YS, Wang H (2017) Humic substances as a washing agent for Cd-contaminated soils. *Chemosphere* 181:461–467
- Nowack B, Sigg L (1997) Dissolution of Fe(III) (hydr) oxides by metal-EDTA complexes. *Geochim Cosmochim Acta* 61:951–963
- Nowack B, Schulin R, Robinson BH (2006) Critical assessment of chelant-enhanced metal phytoextraction. *Environ Sci Technol* 40:5225–5231
- Park B, Son Y (2017) Ultrasonic and mechanical soil washing processes for the removal of heavy metals from soils. *Ultrason Sonochem* 35:640–645
- Pham TD, Shrestha RA, Virkutyte J, Sillanpää M (2013) Recent studies in environmental applications of ultrasound. *J Environ Eng Sci* 8:403–412
- Picó Y (2013) Ultrasound-assisted extraction for food and environmental samples. *TrAC-Trend Anal Chem* 43:84–99
- Rinklebe J, Shaheen SM, El-Naggar A, Wang H, Du Laing G, Alessi DS, Sik Ok Y (2020) Redox-induced mobilization of Ag, Sb, Sn, and Tl in the dissolved, colloidal and solid phase of a biochar-treated and un-treated mining soil. *Environ Int* 140:105754
- Santos EVD, Sáez C, Cañizares P, Martínez-Huitle CA, Rodrigo MA (2016) UV assisted electrochemical technologies for the removal of oxyfluorfen from soil washing wastes. *Chem Eng J* 318:2–9
- Son Y, Cha J, Lim M, Ashokkumar M, Khim J (2011) Comparison of ultrasonic and conventional mechanical soil-washing processes for diesel-contaminated sand. *Ind Eng Chem Res* 50:60–64
- Son Y, Nam S, Ashokkumar M, Khim J (2012) Comparison of energy consumptions between ultrasonic, mechanical, and combined soil washing processes. *Ultrason Sonochem* 19:395–398
- Son Y, Lee D, Lee W, Park J, Hyoung Lee W, Ashokkumar M (2019) Cavitation activity in heterogeneous systems containing fine particles. *Ultrason Sonochem* 58:104599
- Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R, Nowack B (2004) Extraction of heavy metals from soils using biodegradable chelating agents. *Environ Sci Technol* 38:937–944
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51:844–851
- Tsang DCW, Hartley NR (2014) Metal distribution and spectroscopic analysis after soil washing with chelating agents and humic substances. *Environ Sci Pollut Res* 21:3987–3995
- Tsang DCW, Zhang WH, Lo IMC (2007) Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils. *Chemosphere* 68:234–243

- Walkley A (1935) An examination of methods for determining organic carbon and nitrogen in soils. *J Agr Sci* 25:598–609
- Wang J, Jiang J, Li D, Li T, Li K, Tian S (2015) Removal of Pb and Zn from contaminated soil by different washing methods: the influence of reagents and ultrasound. *Environ Sci Pollut Res* 22:20084–20091
- Wang L, Ok YS, Tsang DCW, Alessi DS, Rinklebe J, Wang H, Mašek O, Hou R, O'Connor D, Hou D (2020) New trends in biochar pyrolysis and modification strategies: feedstock, pyrolysis conditions, sustainability concerns and implications for soil amendment. *Soil Use Manage*. <https://doi.org/10.1111/sum.12592>
- Wu P, Cui P, Alves ME, Peijnenburg WJGM, Liu C, Zhou D, Wang H, Ok YS, Wang Y (2019) Interactive effects of rice straw biochar and γ -Al₂O₃ on immobilization of Zn. *J Hazard Mater* 373:250–257
- Xia S, Song Z, Jeyakumar P, Shaheen SM, Rinklebe J, Ok YS, Bolan N, Wang H (2019) A critical review on bioremediation technologies for Cr(VI)-contaminated soils and wastewater. *Crit Rev Environ Sci Technol* 49:1027–1078
- Xu X, Liu X, Li Y, Ran Y, Liu Y, Zhang Q, Li Z, He Y, Xu J, Di H (2017) High temperatures inhibited the growth of soil bacteria and archaea but not that of fungi and altered nitrous oxide production mechanisms from different nitrogen sources in an acidic soil. *Soil Biol Biochem* 107:168–179
- Yoo JC, Beiyuan J, Wang L, Tsang DCW, Baek K, Bolan NS, Ok YS, Li XD (2018) A combination of ferric nitrate/EDDS-enhanced washing and sludge-derived biochar stabilization of metal-contaminated soils. *Sci Total Environ* 616–617:572–582
- Zhai X, Li Z, Huang B, Luo N, Huang M, Zhang Q, Zeng G (2018) Remediation of multiple heavy metal-contaminated soil through the combination of soil washing and in situ immobilization. *Sci Total Environ* 635:92–99
- Zhang W, Huang H, Tan F, Wang H, Qiu R (2010) Influence of EDTA washing on the species and mobility of heavy metals residual in soils. *J Hazard Mater* 173:369–376
- Zhang T, Liu JM, Huang XF, Xia B, Su CY, Luo GF, Xu YW, Wu YX, Mao ZW, Qiu RL (2013) Chelant extraction of heavy metals from contaminated soils using new selective EDTA derivatives. *J Hazard Mater* 262:464–471
- Zhao FJ, Ma Y, Zhu YG, Tang Z, McGrath SP (2015) Soil contamination in China: current status and mitigation strategies. *Environ Sci Technol* 49:750–759
- Zhao T, Zhang K, Chen J, Shi X, Li X, Ma Y, Fang G, Xu S (2019) Changes in heavy metal mobility and availability in contaminated wet-land soil remediated using lignin-based poly(acrylic acid). *J Hazard Mater* 368:459–467
- Zou Z, Qiu R, Zhang W, Dong H, Zhao Z, Zhang T, Wei X, Cai X (2009) The study of operating variables in soil washing with EDTA. *Environ Pollut* 157:229–236
- Zupanc V, Kastelec D, Lestan D, Grcman H (2014) Soil physical characteristics after EDTA washing and amendment with inorganic and organic additives. *Environ Pollut* 186:56–62

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