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Effect of mixed chelators of EDTA, GLDA, and citric acid on bioavailability of residual heavy metals in soils and soil properties

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HIGHLIGHTS

- MC efficiently removed 10.7–60.9% of Cd, Zn, Pb, and Cu from contaminated soils.
- The bioavailability of residual heavy metals in calcareous chelators-washed soil were higher than those without chelators.
- Compared to $FeCl_3$- and EDTA-washing, MC tended to moderate change soil properties.
- The germination and growth of Chinese cabbage in MC-washed soil were the highest.

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ABSTRACT

Soil washing is an effective technology for the remediation of multi-metal contaminated soils. However, bioavailability of residual heavy metals in soils and soil properties could be changed during washing processes. This study investigated the effects of EDTA, $FeCl_3$ and mixed chelators (MC) on bioavailability of residual heavy metals in soils and soil biological properties after soil washing. The results showed that soil washing by chelators successfully decreased the total concentration of heavy metals in soils, while it did not effectively decrease the exchangeable fraction of heavy metals, especially for calcareous contaminated soil. The toxic effects of the washed soils seemed to exhibit higher correlations with the changes in the soil properties such as soil pH and nutrient concentrations. As compared with $FeCl_3$ and EDTA, MC tended to moderately change soil properties (e.g., pH, total N, available N, available P, and exchangeable K, Ca, and Mg). Additionally, MC-washed soil had the least influence on the soil enzymes activities, and had the highest germination and growth of Chinese cabbage. Accordingly, MC is a moderate washing solution in the removal of heavy metals from multi-metal contaminated soils, and had minimal negative effects on soil qualities.

1. Introduction

Heavy metal contamination in soils is one of the major worldwide environmental problems, which is mainly caused by the development of mining industry, waste water irrigation, and sewage sludge application (Luo et al., 2012; Zhang et al., 2013; Zhao et al., 2015). Intensive search of remediation technologies for metal contaminated soil and ways for their safe use for agriculture production have been undergoing in past few decades.

The remediation technologies for metal-contaminated soils include chemical, physical, or biological techniques (Khalid et al., 2017; Song et al., 2017). Chemical techniques, such as soil washing with various chemicals, are effectively useful for remediating contaminated soils (Peters, 1999; Lestan et al., 2008; Mao et al., 2017). Ethylenediaminetetraacetic acid (EDTA) is the most frequently cited chelating agent for the extraction of potentially toxic trace metals from soils, because of its strong chelating ability for different heavy metals (Sun et al., 2001; Zou et al., 2009). In recent years, biodegradable chelators as a promising substitute of EDTA, such as S, S-ethylenediaminedisuccinic acid (EDDS), N, N-Bis(carboxymethyl) glutamic acid (GLDA), citric acid, have emerged because of their relatively strong complexing ability with heavy

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metals in soil washing processes (Yip et al., 2009; Begum et al., 2012; Li et al., 2015; Wang et al., 2016; Beiyuan et al., 2017). Additionally, $FeCl_3$ is also selected as soil-washing chemical for heavy metals-contaminated soils (Li et al., 2015; Guo et al., 2016; Chen et al., 2016), especially, for Cd-contaminated paddy soils because of its Cd-extraction efficiency and cost effectiveness (Makino et al., 2008, 2016).

Although soil washing was an efficient and permanent way of removing heavy metals from contaminated soils, soil properties and bioavailability of residual heavy metals in soils could be changed during washing processes (Jelusic and Lestan, 2014; Wang et al., 2016, 2018). Specifically, soil washing by EDTA decreased silt content but increased clay content, pH value, base saturation and reduced base cations except for Na, and slightly decreased the amount of exchangeable K as compared with the original soil (Zupanc et al., 2014). Remediation by EDTA washing initially reduced the soil DNA content (up to 29%, 30 mmol kg^{-1} EDTA) and changed the structure of microbial population (Jelusic et al., 2013). Chinese cabbage planted in the remediated soil managed to absorb more Pb, Cd, and Zn in their upper parts because of the residual EDTA-metal complexes in remediation soil (Jelusic et al., 2013). Previous study also reported that the concentrations of Cd, Zn, and Cu in grains of *Zea mays* L. grown in washed soils were obviously higher as compared with those in the control treatment (Guo et al., 2013). Additionally, negative effects of the reagents application to soil on plant yield were also reported (Jelusic et al., 2014; Guo et al., 2016). For example, the application of $FeCl_3$ significantly reduced the yield of *Sedum alfredii* H. but increased the metal concentrations in *Zea mays* L.(Guo et al., 2016).

Consequently, there is an increasing interest in minimizing negative effects of soil washing on soil qualities. To enhance the removal efficiency of heavy metals, previous studies on soil washing started to focus on composite washing. Qiu et al. (2010) reported that As, Cd, Cu, Pb, and Zn were removed better with combined Na_2EDTA and oxalate. Li et al. (2015) also reported that Pb and Cd removal efficiencies were increased by using $FeCl_3$ or $CaCl_2$ mixed with citric acid as compared with the single $FeCl_3$, $CaCl_2$, or citric acid washing. Previous study reported that the mixed chelators (EDTA, GLDA, and citric acid) could remove more heavy metals from heavily multi-metal contaminated soils as compared with single EDTA at the same application dose of total chelators (Guo et al., 2018). However, the knowledge of effect of mixed chelators on the variation of soil properties and heavy metal bioavailability in soils after soil washing by these chemicals is still limited.

The objectives of this research were (i) to investigate the chemical fractionation of residual heavy metals in soils by washing with EDTA, $FeCl_3$ and a mixture of EDTA, GLDA, and citric acid at the same total dose of chelators, (ii) to evaluate the variations of soil physicochemical properties by different washing reagents, (iii) to estimate the variations of soil eco-toxicological and soil biochemical properties in washed-soil.

2. Materials and methods

2.1. Soil and chemical chelators

A calcareous contaminated soil ($CaCO_3$ content 18.4%) was collected from 0 to 20 cm layer around the metal smelter in Zhuzhou City, Hunan Province, Southern China. An acid contaminated soil was collected from 0 to 20 cm layer within a plot of a paddy located at the downstream of the Dabaoshan mine area in Shaoguan City, Guangdong Province, Southern China. The collected soil samples were air-dried at room temperature, and sieved using a 2-mm and 0.149-mm sieves for physiochemical analysis and subsequent experiments, respectively. Selected properties of the soils were presented in Table 1.

Na_2-EDTA, citric acid and $FeCl_3$ (analytical reagents grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. GLDA was purchased from Akzo Nobel Chemicals Co., Ltd. It has a relative molecular mass of 351.1, solid content >47%, density $\approx 1.400\ g\ cm^{-3}$. GLDA shows good solubility in aqueous solutions over a wide range of pH values. MC was the solution of EDTA, GLDA, and citric acid, and the molar ratio of EDTA, GLDA, and citric acid was 1:1:3 (Guo et al., 2018).

Table 1
Variations physicochemical characteristics of the tested soil samples before and after varieties washing treatments.

Characteristics	Calcareous contaminated soil					Acid contaminated soil				
	Original	Control	$FeCl_3$	EDTA	MC	Original	Control	$FeCl_3$	EDTA	MC
Sand/silt/clay (%)	62/34/4	63/33/4	61/28/11	61/27/12	63/26/11	15/62/23	16/58/26	15/53/32	16/54/30	16/53/31
pH	7.61 ± 0.03c	7.60 ± 0.05c	6.29 ± 0.02d	9.44 ± 0.06a	8.76 ± 0.01b	4.35 ± 0.03c	4.40 ± 0.02c	2.13 ± 0.03d	5.70 ± 0.03a	4.91 ± 0.02b
Soil organic matter ($g \cdot kg^{-1}$)	79.41 ± 6.87a	82.71 ± 1.43a	82.67 ± 5.73a	85.57 ± 1.64a	89.56 ± 5.72a	26.10 ± 0.43a	26.15 ± 0.74a	26.17 ± 0.59a	24.93 ± 1.12a	24.64 ± 0.97a
CEC	41.51 ± 1.31b	35.85 ± 0.38c	17.52 ± 0.02d	48.2 ± 0.53a	45.96 ± 1.32a	3.80 ± 0.32c	4.32 ± 0.32c	3.65 ± 0.53c	6.96 ± 0.07a	5.13 ± 0.10b
Total N ($g \cdot kg^{-1}$)	4.05 ± 0.18a	3.65 ± 0.26ab	3.14 ± 0.16c	3.29 ± 0.34bc	3.25 ± 0.21bc	2.91 ± 0.12a	2.87 ± 0.31ab	2.40 ± 0.16c	2.50 ± 0.27bc	2.77 ± 0.02abc
Total P ($g \cdot kg^{-1}$)	0.64 ± 0.01a	0.60 ± 0.05a	0.64 ± 00.2a	0.63 ± 0.02a	0.63 ± 0.01a	0.49 ± 0.03a	0.49 ± 0.01a	0.48 ± 0.01a	0.47 ± 0.01a	0.48 ± 0.01a
Total K ($g \cdot kg^{-1}$)	28.53 ± 0.71a	27.00 ± 0.71ab	22.65 ± 1.41c	25.45 ± 1.41b	26.03 ± 0.71ab	24.15 ± 1.41a	24.03 ± 0.71a	23.06 ± 0.41a	22.88 ± 0.59a	22.94 ± 0.71a
Total Mn ($mg \cdot kg^{-1}$)	2873 ± 157a	2797 ± 207a	1770 ± 43c	2022 ± 98b	2042 ± 162b	228 ± 19a	223 ± 23a	188 ± 12b	186 ± 11b	227 ± 21a
Available N ($mg \cdot kg^{-1}$)	120±5c	131±6c	142 ± 11bc	176 ± 13a	164 ± 16ab	154 ± 12c	171 ± 16bc	159±9c	182 ± 11ab	201 ± 11a
Available P ($mg \cdot kg^{-1}$)	16.1 ± 0.55c	18.0 ± 0.4c	3.1 ± 0.1d	40.7 ± 2.2a	35.9 ± 1.9b	9.9 ± 0.5a	8.1 ± 0.0b	8.3 ± 0.2b	8.5 ± 0.1b	7.9 ± 0.1b
Exchangeable K ($mg \cdot kg^{-1}$)	7231 ± 755a	6528 ± 454a	1215 ± 15d	3047 ± 20c	5200 ± 361b	463 ± 71a	393 ± 17ab	277 ± 43c	353±5bc	362 ± 23abc
Exchangeable Ca ($mg \cdot kg^{-1}$)	8628 ± 169a	7807 ± 129a	4697 ± 36b	7653 ± 409a	8040 ± 680a	682 ± 106a	723 ± 15a	158 ± 10b	672 ± 39a	670 ± 22a
Exchangeable Mg ($mg \cdot kg^{-1}$)	171 ± 17a	162 ± 12a	92±7c	137±6b	155 ± 13a	93±7a	86±3a	54±6b	78±5a	82±6a
Exchangeable Na ($mg \cdot kg^{-1}$)	159 ± 30c	86 ± 20c	170±7c	4710 ± 339a	1643 ± 101b	270±8d	312 ± 31d	362 ± 11c	2537±5a	1197 ± 24b

The applying amount of $FeCl_3$, EDTA, and MC was 0.6 mol kg^{-1} for calcareous contaminated soil and 0.06 mol kg^{-1} for acid contaminated soil. MC was the mixed solution of EDTA, GLDA, and citric acid (molar ratio of EDTA, GLDA, and citric acid = 1:1:3). Control treatment was washing with distilled water. The values in the table are Mean ± SD(n = 3). According to Duncan's multiple range test ($p < 0.05$) the means in the same line (same contaminated soil) followed by the same letter were not significantly different.