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ORIGINAL PAPER

Effectiveness of nitrilotriacetic acid (NTA) on cadmium removal in calcareous soil and acidic soil

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Abstract

The use of chelators with high biodegradability is a promising strategy to remove potentially toxic elements (PTEs) from soils by washing. The current study investigated the potential of nitrilotriacetic acid (NTA) to remove Cd from Cd-contaminated soil from Iran (calcareous soil, I_{Cd}) and Belgium (acidic soil, B_{Cd}). Washing tests were carried out with soils artificially contaminated with 2 levels of Cd (20 and 40 mg kg^{-1}), 4 levels of NTA (0, 2, 5, and 15 mmol L^{-1}), different pHs (4, 7, and 10), and different contact times (20, 40, and 60 min). The results showed that the optimal concentrations of NTA were 5 and 2 mmol L^{-1} for I_{Cd} and B_{Cd}, respectively. After using NTA_5 compared to NTA_0, Cd removal at pH 4, 7, and 10 increased by 1, 76, and 80% in I_{Cd20} and 1, 77, and 81% in I_{Cd40}, respectively. These values were 46, 53, and 52% in B_{Cd20} and 32, 64, and 62% in B_{Cd40}, respectively, after using NTA_2. Also, in the first 20 min of the experiment, 95–100% and 75–80% of the maximum extractable Cd were removed from I_{Cd} and B_{Cd}, respectively. Moreover, NTA extracted a higher percentage of Ca, Fe, Al, Zn, and Cu from B_{Cd} compared to I_{Cd} (as an exception, the percentage of Ca extracted at pH 4 was higher in I_{Cd} compared to B_{Cd}). The results showed that the physical/chemical properties of soils affect the washing efficiency and should be taken into account before selecting the type and dose of chelate to remove metals in a given soil.

Keywords Acidic soil · Cadmium fractions · Calcareous soil · Nitrilotriacetic acid · Washing of heavy metals

Introduction

The rapid growth of the human population in recent years has led to an increase in environmental pollution (Xiao et al. 2019). One of the most important global issues is the remediation of metal-contaminated agricultural soils and the protection of safe agricultural productions (Rizwan et al. 2016; Cao and Huang 2017). The study of cadmium (Cd) is of particular importance due to its high chemical activity in the soil and its persistent toxicity (Chen et al. 2018; Rassaei et al. 2020), as this metal can completely disrupt the physiological functions of the plant (Chtouki et al. 2021). Cd accumulates in high quantities in plant tissue (Mehrab et al. 2021; Mehrab et al. 2023) and can easily enter the human food chain.

Soil contamination with Cd can be found in different areas throughout the world and, therefore, in soils with different properties. Certain physicochemical soil properties, such as pH, calcium carbonate content (CC), and organic matter content (OM), have a significant effect on Cd mobility and bioavailability (Meers et al. 2005b; Cheng et al. 2017; Khodaverdiloo et al. 2020; Elhaddad 2020). The solubility of PTEs can create problems in acidic soil with low content of calcium and magnesium (Różyło et al. 2017). Generally, the bioavailability of potentially toxic elements (PTEs) in calcareous soils is lower than in acidic soils at similar contamination levels (Cornu et al. 2014) due to PTE precipitation (Khodaverdiloo et al. 2020; Mehrab et al. 2021). In this condition, metals can also form hydroxide precipitates and enter the solid phase (Curtin and Trolove 2013; Ketrot et al. 2013). Wang et al. (2020b) and Meng et al. (2018), for instance, used Si-Ca-K-Mg and lime in the soil, respectively, and reported reduced mobility of Cd when these amendments were applied. Moreover, the alteration of soil pH can change the stability and charge of the surface

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sites of soil particles (Wang et al. 2013; Wang et al. 2020b). The adsorption reaction of Cd on positively charged soil particles decreases at acidic pH (Wang et al. 2013); in contrast, the Cd adsorption on the soil particles enhances with an increase in pH due to the electronegativity effect on soil particles (Xie et al. 2020). OM can also reduce the dissolution of Cd in the soil by shifting exchangeable Cd and Fe/Mn oxide-bounded Cd to Cd complexed to OM (Van Poucke et al. 2018; Xie et al. 2020).

Soil chemical leaching can clean contaminated soil with high concentrations of PTEs in a short period at a low cost while maintaining soil characteristics for reusability (Dermont et al. 2008). However, the choice of leaching agent is important for reaching high leaching efficiency and good soil quality after remediation. Strong acids and chelating agents are commonly used to remediate PTEs in contaminated soils (Dermont et al. 2008; Luo et al. 2018). The application of strong acids (e.g., HCl, H_2SO_4, H_3PO_4, and HNO_3) can clean the contaminated soil in the shortest possible time but may cause damage to soil structure, organic matter, and surrounding environment (Dermont et al. 2008; Luo et al. 2018). Chelators have a lower impact on soil properties and can be used efficiently on a very wide range of pH (Zupanc et al. 2014). However, ethylenediaminetetraacetic acid (EDTA), one of the most commonly used chelators, has a half-life of 36 days (Meers et al. 2005a), remaining in the soil for a long time and increasing the risks of environmental pollution. In contrast, soil washing using environmentally friendly chelators is recommended (Naghipour et al. 2017; Bai 2018; Xie et al. 2020; Zhong et al. 2021). Biodegradable chelators such as nitrilotriacetic acid (NTA) (Naghipour et al. 2017; Xie et al. 2020) can be a better choice to leach PTEs due to their shorter half-life (0–7 days) and environmental safety (Meers et al. 2004; Bai 2018; Wang et al. 2022). NTA decomposes into CO_2 and NH_3 after a maximum period of 2 weeks and therefore has short-term stability in the soil environment (Bai 2018). Although NTA may be less effective than other reagents such as DTPA, EDTA, and HCl (Mosekiemang and Dikinya 2012; Xiao et al. 2019), it generally has less destructive effects on soil and plants (Jiang et al. 2017). NTA reduces the amount of Cd absorbed by soil particles (Xie et al. 2020).

The present study was performed on soils of Iran (calcareous soil) and Belgium (acidic soil), which have significant differences in their main parameters, to assess Cd removal efficiency in widely differing soil conditions. Therefore, this experiment was performed to study the chemical behavior of NTA on Cd removal as affected by the characteristics of soil and washing parameters, i.e., the concentration of NTA, pH of washing solution (4, 7, and 10), and duration of the washing process (20, 40, 60 min). At the end of the experiment, the concentration of Ca, Fe, Al, Zn, and Cu in the soils was also determined to understand the influence of soil composition and competitive ions in Cd removal. So, this research was carried out to address the following questions: (i) in the soils with similar Cd concentration, how do different characteristics of soils affect toxicity, (ii) which fractions of Cd were removed by NTA (does NTA have the ability to remove the residual form of Cd in soils), (iii) which ions in the soils create the most competition for Cd removal? The answers to these questions will help to achieve the maximum performance of soil Cd removal by sensible choosing NTA in the soil.

Previous studies (including research previously published by the authors (Mehrab et al. 2021)) have shown that NTA chelate can help remove soil Cd by increasing Cd dissolution during the phytoremediation method in calcareous soil. The present study is basic research to understand the details of NTA performance, in order to recommend the application of this chelator in soils with different characteristics of soil texture, pH, OM, etc., to increase the dissolution of Cd along with other methods (such as phytoremediation). The results of this study clarify how differences in soils and, subsequently, the distribution of Cd fractions affect NTA performance on Cd dissolution.

Materials and methods

The methodology of the current research includes the following six steps: (i) collecting Iranian and Belgian soils and analyzing their physical and chemical characteristics, (ii) contaminating the soils with Cd and determining the pseudo-total concentration of Cd, (iii) soil incubation for 3 months and measuring Cd fractions in the soils at the end of incubation pried, (iv) soil washing tests in pH 4, 7, and 10 by pH-stat during times, (v) laboratory analysis of soil to determine element concentration (Ca, Fe, Al, Zn, and Cu) and Cd fractions, as well as analysis of filtrated suspension to measure Cd concentration at the end of experiments, and (vi) statistical analysis of data by SPSS software (Fig. 1).

Soil sampling and contaminated soil preparation

The present study was conducted jointly between Shahid Chamran University of Ahvaz, Iran, and Ghent University, Belgium. To perform the experiments, the non-contaminated soil sample of Iran was transferred to Belgium. A soil sample of the Shahid Chamran University of Ahvaz located in southwestern Iran (48° 65′ 91.12″ E 31° 30′ 53.82″ N) and a soil sample of the area of Flanders in Belgium (3° 10′ 46.44″ E 51° 02′ 15.64″ N) were chosen. Both soils were sampled within a 30-cm depth and passed through a 2-mm sieve before being characterized for their physical and chemical properties. Soil texture was determined by the hydrometric method (Day 1965). The soil pH and electrical conductivity (EC) were determined in 1:5 soil suspension (soil to water)

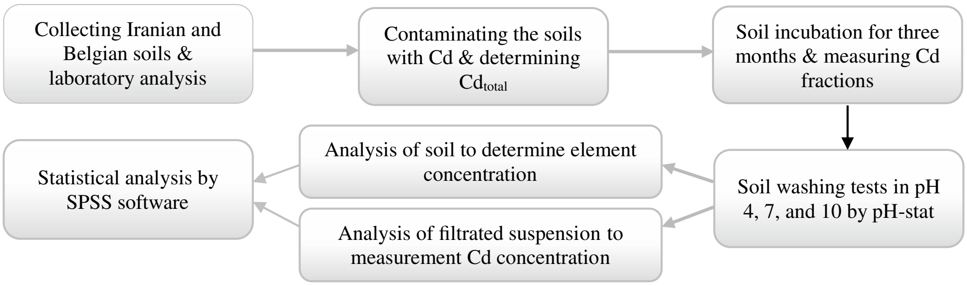

Fig. 1 Flowchart of research methodology structure

Table 1 Physical and chemical properties of the soils used in this study

Parameter	Unit	Value	
		Iran	Belgium
Texture	–	Loamy	Sandy
Clay	(%)	21.4	5.1
Silt	(%)	38.0	1.4
Sand	(%)	40.6	93.5
OM	(%)	0.71	1.98
CCE	(%)	41.3	8.5
CEC	($cmol_+ kg^{-1}$)	12.6	6.06
pH	–	7.7	6.3
EC	($dS m^{-1}$)	2.45	0.81
Ca_{total}	($g kg^{-1}$)	64.02	1.55
Mg_{total}	($g kg^{-1}$)	9.39	0.63
Al_{total}	($g kg^{-1}$)	8.36	1.41
Fe_{total}	($g kg^{-1}$)	10.66	1.81
Cu_{total}	($mg kg^{-1}$)	13.25	14.07
Zn_{total}	($mg kg^{-1}$)	28.89	91.50
Cd_{total}	($mg kg^{-1}$)	0.55	0.51

OM organic matter, *CCE* calcium carbonate equivalent, *CEC* cation exchange capacity, *EC* electrical conductivity

after 2 h of incubation in a shaker at room temperature (Rayment and Higginson 1992). The percentage of calcium carbonate equivalent (CCE) was determined by titration with NaOH after incubation of the soil with acid (Rengasamy and Churchman 1999), and the cation exchange capacity (CEC) was measured by the method of replacement cations with ammonium acetate (Rengasamy and Churchman 1999). The percentage of organic matter (OM) was determined by the Walkley and Black method (Walkley and Black 1934). To measure the pseudo-total concentration of Cd, Zn, Cu, Fe, Al, Ca, and Mg, the digestion method was used with HNO_3 and HCl solutions (Vlarebo 1996), and then, the concentration of these elements was determined using ICP-OES (Vista-MPX). The physical and chemical properties of the soils (Iran and Belgium) are presented in Table 1.

To artificially contaminate the Belgian and Iranian soils, $CdCl_2 \cdot 2.5H_2O$ solutions (20 and 40 ppm) were sprayed on the soils to reach final Cd contamination levels of 20 and 40 mg kg^{-1}. To obtain homogeneous contamination, the contaminated soils were kept in pots at room temperature (25 ± 5 °C) for three months and weighed twice a week to maintain their moisture content at 70% field capacity with the addition of water; soils were also well-mixed after water addition. At the end of the incubation period, contaminated soils of Iran with 20.2 and 40.1 mg kg^{-1} of Cd and contaminated soils of Belgium with 20.6 and 40.3 mg kg^{-1} of Cd were prepared. Therefore, the soils studied included the following: I_{Cd20} (Iranian soil with 20 mg kg^{-1} of Cd), I_{Cd40} (Iranian soil with 40 mg kg^{-1} of Cd), B_{Cd20} (Belgian soil with 20 mg kg^{-1} of Cd), and B_{Cd40} (Belgian soil with 40 mg kg^{-1} of Cd). After the preparation of the contaminated soils, the chemical fractions of Cd in the soil samples were measured by the sequential extraction method of Krishnamurti and Naidu (2000). According to this method, the concentration of Cd is determined in seven fractions: F_1—exchangeable; F_2—carbonate bound; F_3—metal-organic complex bound; F_4—organic bound; F_5—amorphous Fe–Mn oxide bound; F_6—crystalline Fe-Mn oxide bound; F_7—residual (Table 2). The pseudo-total concentration of Cd and Cd fractions was determined by ICP-OES.

Soil washing experiments

To determine the efficiency of NTA on Cd removal from the soils, different concentrations of NTA (0, 2, 5, and 15 mmol L^{-1}) with a solid to liquid ratio of 1:20 (w/v) (Xiao et al. 2019) were added to the soils (I_{Cd20}, I_{Cd40}, B_{Cd20}, B_{Cd40}) in 100-mL beakers. The slurries were stirred at 600 rpm (Niinae et al. 2008), and their pH was adjusted and maintained at 4, 7, and 10 with a pH-stat (Stat Titrino 718) by using NaOH and HCl solutions at room temperature (25 °C ± 1 °C). The experiment slurry was sampled at different times, i.e., 20, 40, and 60 min, and the samples obtained were centrifuged at 6000 rpm for 5 min. Suspensions were thereafter filtered through a 0.45-µm filter, and the Cd content in the filtrate was determined by ICP-OES. Metal removal efficiencies were calculated with Eq. (1):

$$\text{Removal efficiencies (\%)} = \left(C_l \times V_l\right) / \left(C_s \times M_s\right) \times 100, \quad (1)$$

Table 2 Sequential extraction procedure of Cd in the soils (Krishnamurti and Naidu 2000)

Fraction	Reagent	Extraction conditions
F_1—exchangeable	10 mL 1 M NH_4NO_3 (pH 7)	4 h shaking at 25 °C
F_2—carbonate bound	25 mL 1 M CH_3COONa	6 h shaking at 25 °C
F_3—metal-organic complex bound	20 mL 0.1 M $NH_2OH.HCl$ in 0.1 M HNO_3	30 min shaking at 25 °C
F_4—organic bound	5 mL 30% H_2O_2 (pH 2) 3 mL 0.02 M HNO_3	2 h shaking at 25 °C
	3 mL 30% H_2O_2 (pH 2) 1 mL 0.02 M HNO_3	2 h shaking at 25 °C
	Cool, 10 mL 2 M NH_4NO_3 in 20% HNO_3	30 min shaking at 25 °C
F_5—amorphous Fe-Mn oxide bound	20 mL 0.2 M $(NH_4)_2C_2O_4$/2 M $H_2C_2O_4$ (pH 3)	4 h shaking at 25 °C (dark)
F_6—crystalline Fe-Mn oxide bound	25 mL 0.2 M $(NH_4)_2C_2O_4$ (pH 3) in 0.1 M ascorbic acid	30 min shaking at 95°C
F_7—residual	Digestion with HNO_3:$HClO_4$ (2:1)	–

where C_l and C_s are the Cd concentrations in the filtrate (mg L^{-1}) and soil (mg kg^{-1}), respectively; V_l is the volume of washing solution (L) and M_s is the dry mass of the soil (kg).

At the end of the experiments, chemical fractions of Cd in soil samples were measured by ICP-OES to study the effect of NTA on soil Cd fractions changes. Moreover, the pseudo-total concentration of some elements in the soil including Ca, Fe, Al, Zn, and Cu was measured to determine the effect of NTA on their washing. So, after the maximum test time (60 min), the soils were digested by the method of Vlarebo (1996) followed by measurement with an ICP-OES to determine the concentration of Ca, Fe, Al, Zn, and Cu.

Statistical analysis

Statistical analysis of treatments was carried out by one-way ANOVA, and the comparison of means was performed using Duncan's multiple range test at a probability level of 5% in SPSS software. Excel software was also used to draw the graphs.

Results and discussion

Characteristics of the studied soils

The Iranian soil has a loamy texture with the property of calcareous soil (CCE 41.3%), pH 7.7, and low OM (0.71%), whereas the soil of Belgium was sandy soil with a slightly acidic pH of 6.3, a higher OM content (1.98%), and a lower CCE (8.5%) (cfr. Table 1). Both soils had a similar Cd concentration, of around 0.5 mg kg^{-1}, previous to the artificial contamination.

To study the washing of Cd, it is necessary to know the distribution of the different Cd fractions in the soils (Fig. 2). The different characteristics of soil samples of Iran and Belgium caused a significantly different distribution of Cd fractions even though they had a similar Cd content. In the soil of Iran, the highest fraction of Cd was bounded to carbonate (> 60 %), which can be attributed to the high percentage of $CaCO_3$ in this soil (Khodaverdiloo et al. 2020). Due to the low organic matter in this soil, only a small part of Cd was bound to this faction. In contrast, the soil of Belgium had a higher amount of Cd bound to organic matter (> 50%), especially F_3, which is a weak bound (Adelana et al. 2016). Also, the low amount of carbonates in this soil resulted in a reduced Cd fraction bound to carbonates. In addition, due to its different soil texture and higher clay percentage, the residual fraction of Cd in the soil of Iran was higher than that in the soil of Belgium.

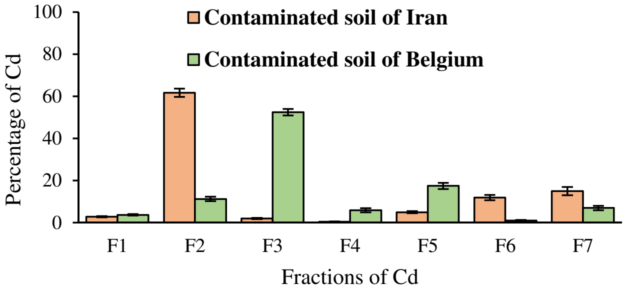

Fig. 2 The distribution of Cd fractions in the contaminated soils of Iran and Belgium (F_1—exchangeable, F_2—carbonate bound, F_3—metal-organic complex bound, F_4—organic bound, F_5—amorphous Fe-Mn oxide bound, F_6—crystalline Fe-Mn oxide bound, F_7—residual)

Effect of pH and NTA on Cd removal from the soils

The efficiency of Cd removal by different NTA concentrations at different pH values in the soils of Iran and Belgium is shown in Fig. 3. According to the results, the removal of Cd in the absence of NTA was only effective at pH 4, with higher efficiency, of around 60%, obtained with the Iranian soil. These results are in line with previous observations that the pH conditions can significantly affect the extraction of Cd (Wang et al. 2019). Interestingly, the addition of NTA

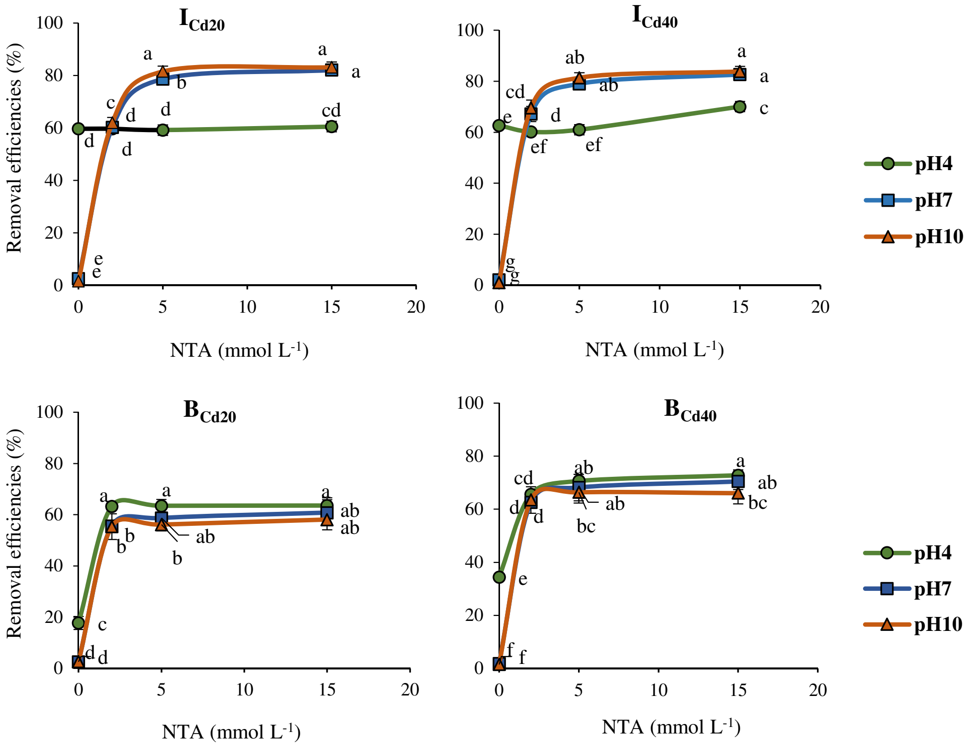

Fig. 3 The efficiency of NTA on Cd removal from the soils of Iran and Belgium in different pH. Different letters show a significant difference according to Duncan's test at 5% probability level (mean ± standard deviation, *n* = 3)

to the washing solution at pH 4 had a negligible effect on Cd removal in the Iranian soil, with only a slight increase in efficiency when using the highest concentration of NTA in the most contaminated soil. These results can be attributed to the increased solubility of $CaCO_3$ in the soil under this acidic pH. In the presence of high Ca concentrations, NTA tends to form chelates with this ion and shows a reduced tendency to form chelates with Cd (Wang et al. 2016). Under acidic conditions, soil PTEs are converted mainly from Fe/Mn oxide bound and carbonate bound fractions to exchangeable and soluble fractions, but organic and residual fractions of PTEs are not released in these conditions (Wang et al. 2020a). As seen in the soil of Belgium, due to the high percentage of Cd bound to the organic matter in F_3 and F_4 (Fig. 2), the percentage of Cd removal at pH 4 was lower than that in the soil of Iran (Fig. 3).

At pH 7 and 10 in the soil of Iran, the efficiency of Cd removal increased from 1–2% to 83–84% with increasing NTA concentrations, regardless of the initial Cd concentration in the soil (Fig. 3). These results can be attributed to the lack of competition between Ca and Cd due to the precipitation of Ca as $CaCO_3$ at high pH values. Also, the limited extraction efficiency of NTA_2 can be attributed to the adsorption of NTA onto soil particles or complexation with other ions in the soil such as Ca, Mg, Fe, and Al (Wang et al. 2016). Increasing the concentration of NTA provides more binding sites that facilitate the formation of Cd-NTA complexes and ultimately increase the extraction of Cd in the soil (Wang et al. 2016; Jiang et al. 2017).

The results of the study showed that NTA efficiency was lower for Cd removal in the Belgian soil, with a maximum efficiency of 60% and 70% for B_{Cd20} and B_{Cd40}, respectively. Nevertheless, similar behavior of Cd removal efficiency increase with increasing NTA applications up to NTA_5 compared to NTA_0 was observed for both soils, while a further increase of NTA concentration to 15 mmol L^{-1} did not increase the washing efficiency (Fig. 3). However, NTA_2 seemed to be sufficient to reach the highest washing efficiencies in the Belgian soil, which can be related to its lower $CaCO_3$ content, as explained above. These results are similar to the studies of Xiao et al. (2019) and Xie et al. (2020). They reported that, after washing off most of the Cd extractable in the soil by NTA, adding more NTA did not have a positive effect. Studies by Xiao et al. (2019) on the effects of EDTA, NTA, HCl, and other washing solutions at a ratio of 1:20 (soil to chelator) on Cd and Zn removal showed that, after the application of 10 mmol L^{-1} of NTA, more than 60% of Cd was removed from the soil, while this amount reached only about 70% by adding 30 mmol L^{-1} of NTA. However, the effect of chelating agent application in the soil can be different due to the presence of various factors influencing the removal of metals as well as the interaction of chelating agents with other elements in the soil.

Effect of washing time on Cd removal from the soils

The effect of time on Cd removal in the soils of Iran and Belgium was assessed for the best conditions for each soil,

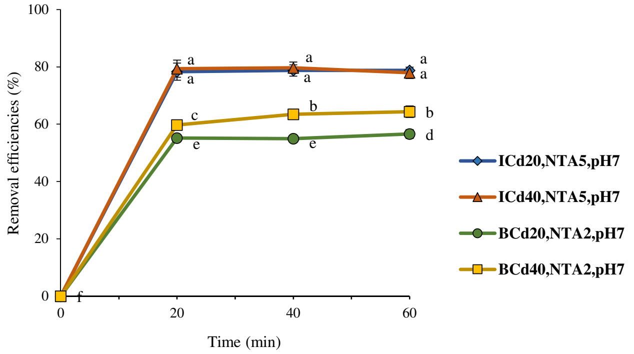

Fig. 4 Variation of the efficiency of NTA on Cd removal with time from the soils of Iran and Belgium. Different letters show a significant difference according to Duncan's test at 5% probability level (mean ± standard deviation, *n* = 3)

i.e., NTA5/pH 7 for the Iranian soil and NTA_2/pH_7 for the Belgian soil (Fig. 4). Even though pH 10 and pH 4 gave slightly better results than pH 7 for I_{Cd20} and B_{Cd20}, respectively (Fig. 3), the difference was not deemed important enough to justify such a drastic change in pH during treatment, especially as the Iranian and Belgian soil's natural pH is already close to 7 (Table 1)—one being 0.7 points above and the other 0.7 points below neutral pH.

The shortest studied duration, of 20 min, was already enough for reaching high washing efficiencies in both soils, with a slight improvement in the results of B_{Cd40} when increasing this to 40 min. Most of the Cd concentration in the soil of Iran is in the form of F_2 (Fig. 2), and less time is required to remove it from the soil due to the low stability of this fraction as studies have shown that F_1 and F_2 are among the most available fractions (Xiao et al. 2019). In contrast, a slight increase in Cd removal in the soil of Belgium was observed with increasing time because most of its Cd is bound to organic matter (Fig. 2), which involves various reactions including ion exchange, chelation, and adsorption (Van Poucke et al. 2018; Xie et al. 2020), yielding a more stable fraction. Part of the results can be attributed to the mechanism of interaction between chelator and PTEs (Li et al. 2018; Zhang et al. 2013). The process of extracting PTEs consists of a fast thermodynamic reaction between PTEs and chelator, which can eliminate the weak bond of PTEs with the soil (F_1 and F_2) and convert them into soluble forms or dissolution of metals in complex compounds consisting of PTEs bonded to Fe/Mg oxides and organic matters (F_3 and F_5).

These results are confirmed by the ones presented in Fig. 5, which shows the proportion of Cd fractions at the end of the experiment in the soils of Iran and Belgium using NTA_5 and NTA_2, respectively. According to the results, the proportion of F_7 in the soils, especially in the soil of Iran, was the highest while F_1 and F_2 were almost eliminated. After the residual fraction (F_7), the fraction bonded to OM (F_3) in the soil of Belgium and the fraction bound to crystalline Fe-Mn oxide (F_6) in the soil of Iran had the highest relative percentage in these soils.

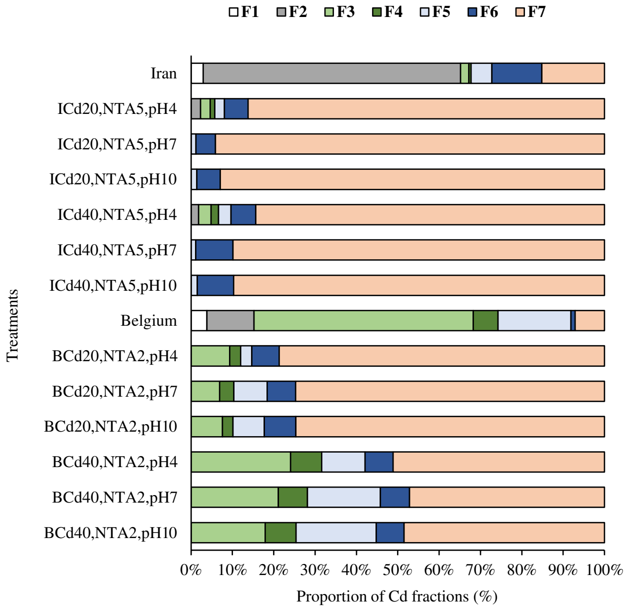

Fig. 5 The proportion of Cd fractions in the soils of Iran and Belgium. F_1—exchangeable, F_2—carbonate bound, F_3—metal-organic complex bound, F_4—organic bound, F_5—amorphous Fe-Mn oxide bound, F_6—crystalline Fe-Mn oxide bound, F_7—residual. Different letters show the significant difference according to Duncan's test at 5% probability level (mean ± standard deviation, *n* = 3)

Effect of soil washing with NTA on the removal of other metals

In general, for the chelate formation with NTA, some metals such as Ca, Mg, and Mn have lower equilibrium constants than other metals such as Cd, Fe, Al, Zn, and Cu (Gong et al. 2009). Meers et al. (2008) and Begum et al. (2013) reported that Ca, Fe, and Al can reduce the efficiency of heavy metal mobility by competition for creating complexation with the chelator. Ca especially interferes in the chelate formation of NTA with Cd when present in high concentrations, as is the case for the Iranian soil used in this study. Therefore, in the present study, due to higher concentrations and possible competition of Fe, Al, Cu, and Zn with Cd for the formation of complexes with NTA, the concentrations of these metals in the soil were also investigated.

After soil washing with NTA, the concentration of Ca in the soil of Iran decreased at different pHs, being more significant at pH 4 due to the acidic conditions and consequent dissolution of soil $CaCO_3$. In the present study, the application of NTA_{15} caused a significant decrease in Ca concentration in the soil of Iran at all pH levels, as the percentage of Ca at pH 4, 7, and 10 was 43, 73, and 74% in I_{Cd20} and 26, 80, and 85% in I_{Cd40}, respectively, relative to the concentration before washing (100%) (Fig. 6). In the soil of Belgium, the application of NTA_{15} in all pHs also successfully removed a large part of Ca and was more effective than in the Iranian soil because the amount of Ca was already low, enabling NTA_{15} to remove most of the exchangeable Ca from the soil. As a result, the percentage of Ca at pH 4, 7, and 10 was 62, 63, and 64% in B_{Cd20} and 57, 57, and 60% in B_{Cd40}, respectively (Fig. 6). Therefore, NTA can remove Ca from the soil. According to Wang et al. (2016) report, the exchangeable Ca, Mg, K, and Na in the soil decreased significantly after soil washing by chelators. Besides, in the absence of NTA, the difference between the amount of Ca at pH 4 and that at pH 7 and 10 is more noticeable in the soil of Iran compared to the soil of Belgium. Similarly, Wang et al. (2020a) found that, by reducing soil pH from 7.5 to 5, the concentration of Ca released from calcareous soils increased by more than 10-fold compared to non-calcareous soils. They reported that, in calcareous soils, since most of Ca is bound to the soil carbonate, reducing the pH dissolves $CaCO_3$ in the soil and releases large amounts of Ca.

The results showed that NTA worked well in extracting Fe and Al from the soils, especially in the soil of Belgium. The application of NTA_{15} at pH 4, 7, and 10 removed 30, 25, and 24% of Fe and 10, 8, and 7% of Al from I_{Cd20}, as well as 34, 29, and 27% of Fe and 20, 14, and 12% of Al from I_{Cd40} (Fig. 7). These values were 62, 59, and 36% of Fe and 66, 64, and 42% of Al in B_{Cd20} and 59, 55, and 46% of Fe and 71, 65, and 60% of Al in B_{Cd40} (Fig. 7). The effectiveness of NTA in removing these metals was minimized by increasing pH. Although NTA was more successful in removing Fe compared to Al in the soils, both metals showed a similar tendency after using NTA. These results are similar to the experimental results of Gong et al. (2009). They reported that NTA caused a significant increase in Fe and Al removal in acidic pH in the soil, as well as a decrease in their removal with increasing pH to 7, but the amount of Fe and Al removed from the soil was still significantly higher than in the condition without NTA. In addition, according to the results, despite the higher concentration of Fe and Al in the soil of Iran (Table 1), a higher percentage of these metals was removed from the soil of Belgium. This is due to the crystalline (insoluble) forms of these metals in the soil of Iran. As can be seen in Fig. 2, the percentage of Fe/Mn oxides in amorphous form (F_5) in the soil of Belgium is higher than in the soil of Iran; in contrast, the percentage of Fe/Mn oxides in crystalline form (F_6) in the soil of Iran is higher than in the soil of Belgium. de Santiago et al. (2008) also reported that poorly crystallized iron oxides are part of plant absorbable Fe. Therefore, Fe in amorphous Fe/Mn oxide form (F_5) is easier to wash compared to Fe in crystalline Fe/Mn oxides form (F_6).

According to the results of Fig. 7, the lowest percentages of Zn and Cu were observed after the application of NTA_{15}. The use of NTA_{15} at pH 4, 7, and 10 removed 45, 41, and 33% of Zn and 63, 55, and 58% of Cu from I_{Cd20}, as well as 41, 37, and 26% of Zn and 59, 50, and 45% of Cu from I_{Cd40} (Fig. 7). In the soil of Iran, the percentage of Cu washed was higher than Zn because research has shown that most of Zn is in the residual fraction in this soil (Karimi et al. 2019; Rassaei et al. 2020) and other alkaline soils (Xiao et al. 2019), which reduces its leaching (Adamo et al. 2018). In contrast, in the soil of Belgium, a higher percentage of Zn compared to Cu was removed from the soil, which is probably due to the acidic pH of this soil, the presence of more organic matter, and higher biological availability of Zn in this soil (Polettini et al. 2009; Lian Svendsen et al. 2011), so probably a lower percentage of Zn was present in the residual fraction. However, the difference between the percentages removed of Zn and Cu decreased due to the use of NTA in the soil. The values of metals washed after

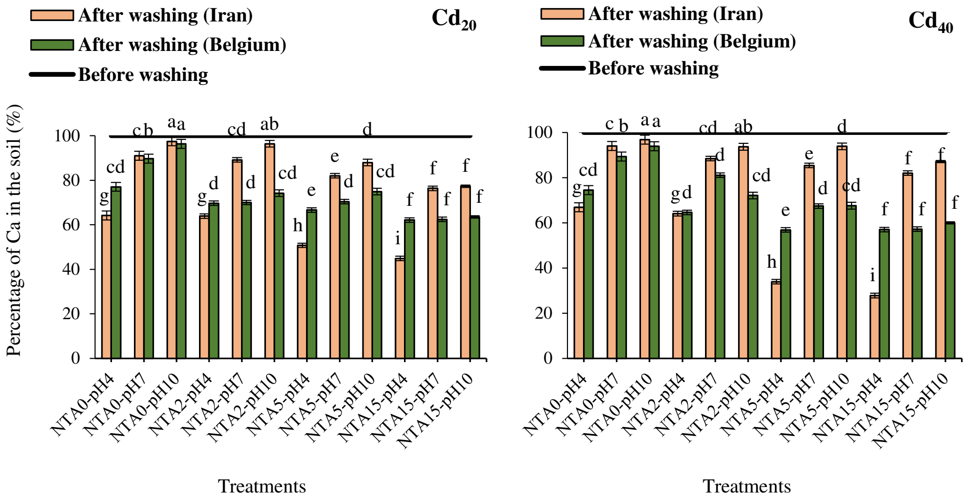

Fig. 6 The efficiency of NTA on Ca removal from the soils of Iran and Belgium at the end of the experiment. Different letters show a significant difference according to Duncan's test at 5% probability level (mean ± standard deviation, $n = 3$)

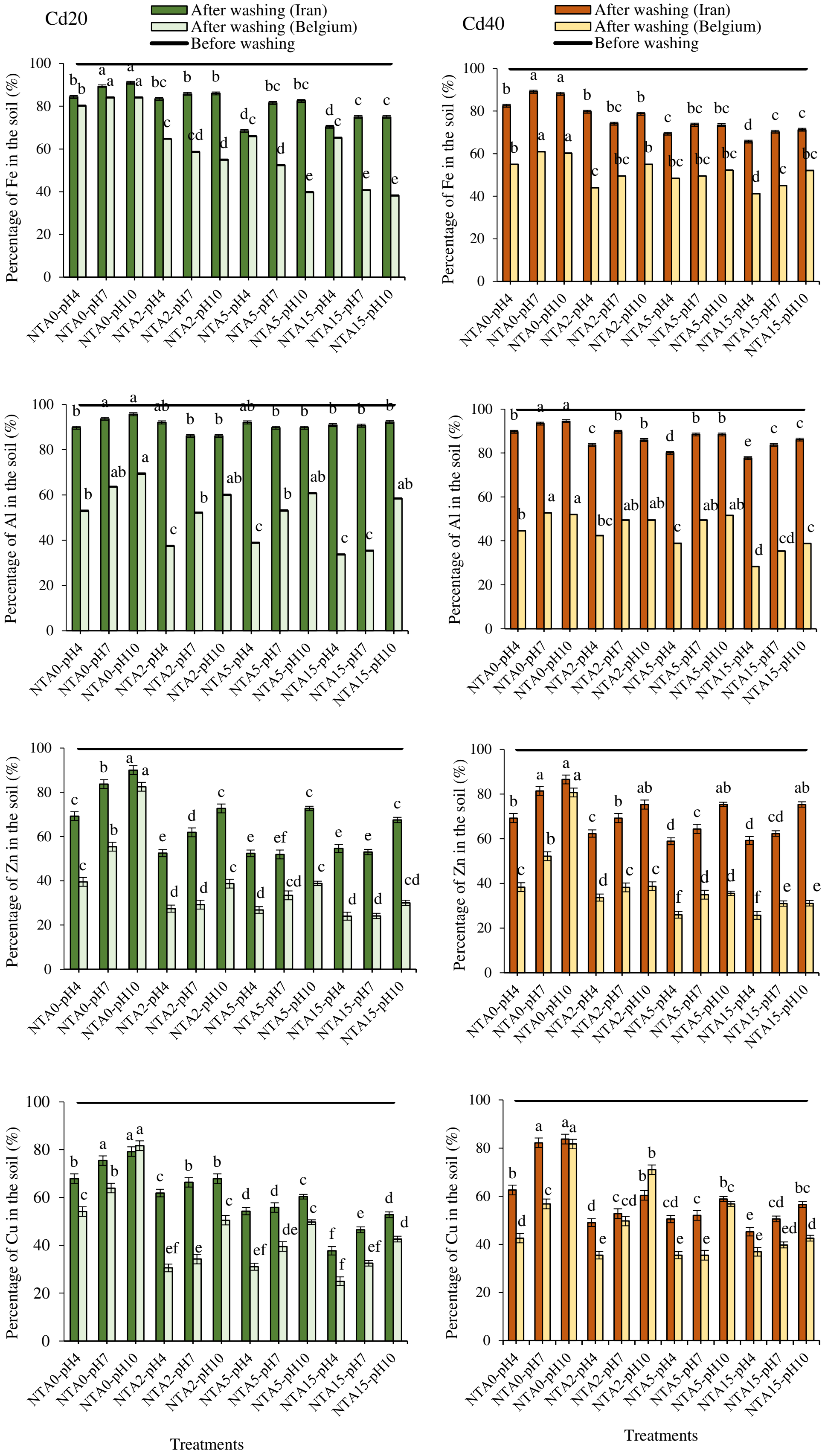

Fig. 7 The efficiency of NTA on Fe, Al, Zn, and Cu removal from the soils of Iran and Belgium at the end of the experiment. Different letters show a significant difference according to Duncan's test at 5% probability level (mean ± standard deviation, $n = 3$)

using NTA_{15} at pH 4, 7, and 10 were 76, 74, and 70% for Zn in B_{Cd20} and 74, 69, and 68% for Zn in B_{Cd40}. These values were 71, 67, and 58% of Cu in B_{Cd20} and 63, 65, and 54% of Cu in B_{Cd40} (Fig. 7). These results are consistent with studies on acidic soils in Hamburg (Brümmer 1986) and Belgium (Horckmans et al. 2006). The sequence of metal mobility in soil was Cd>Zn>Cu>Pb and Cd>Zn>Pb>Cu in the studies conducted by Brümmer (1986) and Horckmans et al. (2006), respectively.

In general, studies have shown that the chemical activity of Zn is lower than some other metals such as Cd, and Zn complexes with chelate are less stable (Shaheen et al. 2013; Naghipour et al. 2017; Xiao et al. 2019) so less Zn is leached from the soil under the influence of NTA. Xiao et al. (2019) showed that using 100 mL L^{-1} of NTA in the soil (with a solid/liquid ratio of 1:20 (w/v)) caused 6 times more efficiency on Cd removal compared to Zn removal. Also, Fe and Al may compete with Cd for bounding to NTA and leaching from the soil, but there is no strong competition for Zn compared to Cd to form an NTA-metal complex, and NTA is more likely to form a chelate with Cd. Naghipour et al. (2017) also reported that the extraction of Cd, Pb, and Zn from contaminated calcareous soils by NTA and EDTA was Cd > Zn > Pb and Pb > Cd > Zn, respectively.

Conclusion

The effect of NTA on Cd removal in the soil of Iran and Belgium was investigated. In general, the efficiency of Cd removal in the soils was significantly affected by the NTA concentration and pH and less by the washing time. The results showed that the effectiveness of NTA on Cd removal at 5 and 2 mmol L^{-1} NTA was optimal for the soils of Iran and Belgium, respectively, and increasing NTA application did not result in a significant improvement in Cd removal. This was due to the presence of part of Cd in the soil residual fraction, a more recalcitrant fraction to extraction, and the increased competition of other metals to form chelates with NTA when using it at a higher concentration. In the soil of Iran, no significant change in Cd removal was observed with time (20 to 60 min), while Cd removal efficiency slightly increased with increasing time in the soil of Belgium. These results can be attributed to the bonding of Cd with carbonates (> 60%) in the soil of Iran, as this fraction of Cd is released more easily than the Cd bonded with organic matter and Fe/Mn oxides, more present in the Belgian soil. The best Cd removal efficiency was observed in the soil of Belgium at acidic pH, which decreased with increasing pH. However, when adding NTA, there was no significant difference in Cd removal between pH 4 and 7, so pH 7 was chosen as the optimal condition, being close to the natural soil pH of Belgium. In contrast, in the soil of Iran, the lowest Cd removal efficiency was obtained at acidic pH, and the removal efficiency was higher at pH 7 and 10. These conflicting results were due to the high competition of Ca with Cd in acidic pH for the formation of chelates with NTA in the soil of Iran. After NTA application in the soils, a higher percentage of Fe, Al, Zn, and Cu was also removed from the soil of Belgium compared to the soil of Iran. Because the soil of Belgium has a quite light texture and low CEC, these metals are in more active and more accessible fractions in the soil, so they are easier to wash. Therefore, the use of NTA in soils containing $CaCO_3$ and neutral and higher pH is recommended to increase the dissolution of Cd. NTA can be used more efficiently in calcareous soils with a medium texture compared to in acidic soils with a light texture to increase Cd solubility and achieve higher efficiency of some methods such as phytoremediation. Future perspectives in research can address the potential recovery and re-use of NTA in addition to further identifying optimal soil-specific washing conditions in practice.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

References

Adamo P, Agrelli D, Zampella M (2018) Chemical speciation to assess bioavailability, bioaccessibility and geochemical forms of potentially toxic metals (PTMs) in polluted soils. In: Vivo BD, Belkin HE, Lima A (eds) Environmental geochemistry. Elsevier, pp 153–194

Adelana AO, Oluwatosin GA, Agunbiade C, Are KS, Adeyolanu OD (2016) Distributions of cadmium and lead in peri-urban wetlands as influenced by soil organic matter, clay fraction, and moisture content. Cogent Food Agric 2:1159406

Bai W (2018) Effects of application of NTA and EDTA on accumulation of soil heavy metals in chrysanthemum. IOP Conference Series: Earth and Environmental Science. IOP Publishing, p 012175

Begum ZA, Rahman IM, Sawai H, Mizutani S, Maki T, Hasegawa H (2013) Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soils. Water Air Soil Pollut 224:1–21

Brümmer G (1986) Heavy metal species, mobility and availability in soils. In: Bernhard M, Brinckman FE, Sadler PJ (eds) The importance of chemical "speciation" in environmental processes. Springer, Berlin, pp 169–192

Cao Q, Huang Z (2017) Review on speciation analysis of heavy metals in polluted soils and its influencing factors. Ecol Sci 36:222–232

Chen H, Yang X, Wang P, Wang Z, Li M, Zhao FJ (2018) Dietary cadmium intake from rice and vegetables and potential health risk: a case study in Xiangtan, southern China. Sci Total Environ 639:271–277

Cheng M, Wang A, Tang C (2017) Ammonium-based fertilizers enhance Cd accumulation in Carpobrotus rossii grown in two soils differing in pH. Chemosphere 188:689–696

Chtouki M, Naciri R, Soulaimani A, Zeroual Y, El Gharous M, Oukarroum A (2021) Effect of cadmium and phosphorus interaction on tomato: chlorophyll a fluorescence, plant growth, and cadmium translocation. Water Air Soil Pollut 232:1–11

Cornu J, Elhabiri M, Ferret C, Geoffroy V, Jezequel K, Leva Y, Lollier M, Schalk IJ, Lebeau T (2014) Contrasting effects of pyoverdine on the phytoextraction of Cu and Cd in a calcareous soil. Chemosphere 103:212–219

Curtin D, Trolove S (2013) Predicting pH buffering capacity of New Zealand soils from organic matter content and mineral characteristics. Soil Res 51:494–502

Day PR (1965) Particle fractionation and particle-size analysis. In: Blac CA (ed) Methods of soil analysis: part 1 physical and mineralogical properties, including statistics of measurement and sampling. Soil Science Society of America, Madison, pp 545–567

de Santiago A, Díaz I, del Campillo MC, Torrent J, Delgado A (2008) Predicting the incidence of iron deficiency chlorosis from hydroxylamine-extractable iron in soil. Soil Sci Soc Am J 72:1493–1499

Dermont G, Bergeron M, Mercier G, Richer-Laflèche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. J Hazard Mater 152:1–31

Elhaddad E (2020) Sportive removal of cadmium (II) pollutant by modified Stevia plant: kinetics and sorption studies. Arab J Geosci 13:1–9

Gong Z, Liu Y, Jiang Y (2009) Apply EDTA and NTA to extract Fe and Al ions from sewage sludges: batch study. 3rd International Conference on Bioinformatics and Biomedical Engineering. IEEE, pp 1–4

Horckmans L, Swennen R, Deckers J (2006) Geochemical and mineralogical study of a site severely polluted with heavy metals (Maatheide, Lommel, Belgium). Environ Geol 50:725–742

Jiang J, Yang M, Gao Y, Wang J, Li D, Li T (2017) Removal of toxic metals from vanadium-contaminated soils using a washing method: reagent selection and parameter optimization. Chemosphere 180:295–301

Karimi A, Moezzi A, Chorom M, Enayatizamir N (2019) Chemical fractions and availability of Zn in a calcareous soil in response to biochar amendments. J Soil Sci Plant Nutr 19:851–864

Ketrot D, Suddhiprakarn A, Kheoruenromne I, Singh B (2013) Interactive effects of iron oxides and organic matter on charge properties of red soils in Thailand. Soil Research 51:222–231

Khodaverdiloo H, Han FX, Hamzenejad Taghlidabad R, Karimi A, Moradi N, Kazery JA (2020) Potentially toxic element contamination of arid and semi-arid soils and its phytoremediation. Arid Land Res Manag 34:361–391

Krishnamurti GS, Naidu R (2000) Speciation and phytoavailability of cadmium in selected surface soils of South Australia. Soil Res 38:991–1004

Li Z, Wu L, Luo Y, Christie P (2018) Changes in metal mobility assessed by EDTA kinetic extraction in three polluted soils after repeated phytoremediation using a cadmium/zinc hyperaccumulator. Chemosphere 194:432–440

Lian Svendsen M, Steinnes E, Blom HA (2011) Partitioning of Zn, Cd, Pb, and Cu in organic-rich soil profiles in the vicinity of a zinc smelter. Chem Speciat Bioavailab 23:189–200

Luo J, Cai L, Qi S, Wu J, Gu XS (2018) Influence of direct and alternating current electric fields on efficiency promotion and leaching risk alleviation of chelator assisted phytoremediation. Ecotoxicol Environ Saf 149:241–247

Meers E, Hopgood M, Lesage E, Vervaeke P, Tack F, Verloo M (2004) Enhanced phytoextraction: in search of EDTA alternatives. Int J Phytoremediation 6:95–109

Meers E, Ruttens A, Hopgood M, Samson D, Tack F (2005) Comparison of EDTA and EDDS as potential soil amendments for enhanced phytoextraction of heavy metals. Chemosphere 58:1011–1022

Meers E, Tack F, Verloo M (2008) Degradability of ethylenediaminedisuccinic acid (EDDS) in metal contaminated soils: implications for its use soil remediation. Chemosphere 70:358–363

Meers E, Unamuno V, Vandegehuchte M, Vanbroekhoven K, Geebelen W, Samson R, Vangronsveld J, Diels L, Ruttens A, Laing GD, Tack F (2005) Soil-solution speciation of Cd as affected by soil characteristics in unpolluted and polluted soils. Environ Toxicol Chem: Int J 24:499–509

Mehrab N, Chorom M, Norouzi Masir M, Biswas JK, Fernandes de Souza M, Meers E (2023) Impact of soil treatment with nitrilo triacetic acid (NTA) on Cd fractionation and microbial biomass in cultivated and uncultivated calcareous soil. J Environ Health Sci Eng 21:1–14

Mehrab N, Chorom M, Norouzi Masir M, Fernandes de Souza M, Meers E (2021) Alteration in chemical form and subcellular distribution of cadmium in maize (*Zea mays* L.) after NTA-assisted remediation of a spiked calcareous soil. Arab J Geosci 14:1–14

Meng J, Zhong L, Wang L, Liu X, Tang C, Chen H, Xu J (2018) Contrasting effects of alkaline amendments on the bioavailability and uptake of Cd in rice plants in a Cd-contaminated acid paddy soil. Environ Sci Pollut Res 25:8827–8835

Mosekiemang T, Dikinya O (2012) Efficiency of chelating agents in retaining sludge-borne heavy metals in intensively applied agricultural soils. Int J Environ Sci Technol 9:129–134

Naghipour D, Jaafari J, Ashrafi SD, Mahvi AH (2017) Remediation of heavy metals contaminated silty clay loam soil by column extraction with ethylenediaminetetraacetic acid and nitrilo triacetic acid. J Environ Eng 143:04017026

Niinae M, Nishigaki K, Aoki K (2008) Removal of lead from contaminated soils with chelating agents. Mater Trans 49:2377–2382

Polettini A, Pomi R, Calcagnoli G (2009) Assisted washing for heavy metal and metalloid removal from contaminated dredged materials. Water Air Soil Pollut 196:183–198

Rassaei F, Hoodaji M, Abtahi SA (2020) Fractionation and mobility of cadmium and zinc in calcareous soils of Fars Province. Iran Arab J Geosci 13:1–7

Rayment G, Higginson FR (1992) Australian laboratory handbook of soil and water chemical methods. Inkata Press, Melbourne

Rengasamy P, Churchman G (1999) Cation exchange capacity, exchangeable cations and sodicity. In: Peverill KI, Sparrow LA, Reuter DJ (eds) Soil analysis an interpretation manual. CSIRO Publishing, Melbourne, pp 147–157

Rizwan M, Ali S, Adrees M, Rizvi H, Zia-ur-Rehman M, Hannan F, Qayyum MF, Hafeez F, Ok YS (2016) Cadmium stress in rice: toxic effects, tolerance mechanisms, and management: a critical review. Environ Sci Pollut Res 23:17859–17879

Różyło K, Świeca M, Gawlik-Dziki U, Stefaniuk M, Oleszczuk P (2017) The potential of biochar for reducing the negative effects of soil contamination on the phytochemical properties and heavy metal accumulation in wheat grain. Agric Food Sci 26:34–46

Shaheen SM, Tsadilas CD, Rinklebe J (2013) A review of the distribution coefficients of trace elements in soils: influence of sorption system, element characteristics, and soil colloidal properties. Adv Colloid Interf Sci 201:43–56

Van Poucke R, Ainsworth J, Maeseele M, Ok YS, Meers E, Tack F (2018) Chemical stabilization of Cd-contaminated soil using biochar. Appl Geochem 88:122–130

Vlarebo VRB (1996) Flemish soil remediation decree ratified by the Flemish government on 22/2/1995. Translated from Dutch

Walkley A, Black IA (1934) An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci 37:29–38

Wang G, Zhang S, Xu X, Zhong Q, Zhang C, Jia Y, Li T, Deng O, Li Y (2016) Heavy metal removal by GLDA washing: optimization, redistribution, recycling, and changes in soil fertility. Sci Total Environ 569:557–568

Wang K, Liu Y, Song Z, Khan ZH, Qiu W (2019) Effects of biodegradable chelator combination on potentially toxic metals leaching efficiency in agricultural soils. Ecotoxicol Environ Saf 182:109399

Wang T, Liu W, Xiong L, Xu N, Ni J (2013) Influence of pH, ionic strength and humic acid on competitive adsorption of Pb (II), Cd (II) and Cr (III) onto titanate nanotubes. Chem Eng J 215:366–374

Wang X, de Souza MF, Li H, Qiu J, Ok YS, Meers E (2022) Biodegradation and effects of EDDS and NTA on Zn in soil solutions during phytoextraction by alfalfa in soils with three Zn levels. Chemosphere 292:133519

Wang Y, Ying Y, Lu S (2020) Si-Ca-K-Mg amendment reduces the phytoavailability and transfer of Cd from acidic soil to rice grain. Environ Sci Pollut Res 27:33248–33258

Wang Z, Jia M, Li Z, Liu H, Christie P, Wu L (2020) Acid buffering capacity of four contrasting metal-contaminated calcareous soil types: changes in soil metals and relevance to phytoextraction. Chemosphere 256:127045

Xiao R, Ali A, Wang P, Li R, Tian X, Zhang Z (2019) Comparison of the feasibility of different washing solutions for combined soil washing and phytoremediation for the detoxification of cadmium (Cd) and zinc (Zn) in contaminated soil. Chemosphere 230:510–518

Xie X, Yang S, Liu H, Pi K, Wang Y (2020) The behavior of cadmium leaching from contaminated soil by nitrilotriacetic acid: implication for Cd-contaminated soil remediation. Water Air Soil Pollut 231:1–12

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

Zhong Q, Zhang S, Pan X, Wang G, Xu X, Li T, Zhou W, He Y, Luo L, Liu Y, Liu Y (2021) Efficiency and comprehensive risk assessment of soil Pb and Cd by washing technique with three biodegradable eluents. Environ Sci Pollut Res 28:1–14

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