



Effect of co-existence of organic acids in the single and competitive adsorption of Cd, Cu, Ni, and Zn to the nanoparticle-treated vineyard soils

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Abstract

Purpose Organic acids in the soil can alter the effectiveness of stabilizers used in contaminated soil remediation.

Methods The influence of the aluminum oxide (Al₂O₃) and titanium dioxide (TiO₂) nanoparticles at the rate of 2% on the adsorption of Cd, Cu, Ni, and Zn with and without the co-existence of organic acids (10 mmol citric and malic acids) was investigated under single (containing only one potentially toxic element (PTE)) and competitive (containing all studied PTE) systems.

Results In the absence of organic acids and in both systems and all treatments Cu was more strongly adsorbed, while the Ni was the least adsorbed PTE in all treatments and in presence and absence of organic acids. In general, the application of both organic acids separately decreased the adsorption capacity of the control (untreated soil having no nanoparticles) and nanoparticles-treated soils for PTEs in both systems, whereas this reduction was more pronounced with citric acid treatment. Based on the Freundlich distribution coefficients, in the presence of both citric and malic acids and especially malic acid, Cd had higher adsorption in TiO₂-treated soils, while other PTEs had differed in different treatments in both systems. This suggests that Cd might be more stabilized in presence of organic acids and TiO₂ nanoparticles and that poses a less ecotoxicological threat. The results of speciation at calculated equilibrium pH indicated low adsorption of Cd, Ni, Zn, and Cu in single and Ni in the competitive systems from the control soils in presence of citric acid.

Conclusion These findings highlight the importance of determining the fate and interactions of organic and PTEs coexisting in agricultural soils amended with nanoparticles.

Keywords Calcareous soils · Contaminated soils · Citric acid · Malic acid · Soil amendments

1 Introduction

Contamination of soils with potentially toxic elements (PTEs) from various sources harms plants and soil microorganisms. Cadmium, Cu, Ni, and Zn are PTEs that, if present in excess

in the soil, cause contamination in the soil and water and cause problems after entering the human food chain. The bioaccumulation of PTEs into the food chain results in health problems for humans (Alloway 2013). Therefore, effective, safe, cost-effective, and non-destructive methods for remediation of contaminated soils with PTEs are necessary (Beiyuan et al. 2016; Kumar et al. 2019; Baruah et al. 2020). There are several ways to reduce the contamination and bioavailability of these PTEs, and adsorption is a simple and most common method in reducing various contaminants from water, waste, and soil. Methods of stabilization and storage of PTEs in soil include chemical stabilization (Wei et al. 2014; Pu et al. 2017) and uptake by plants (Zhang et al. 2013). Other methods included enhancing the removal of PTEs in the soil using organic acids (Astuti et al. 2016) and finally washing them out of the soil profile (Xu et al. 2014) and combining the above methods (Marques et al. 2009; Komárek et al. 2013). However, it has also been noted that some PTEs have less sorption in

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the presence of organic acids, most likely as a result of the blockage of surface sites. Depending on their qualities through various processes, such as site competition, organic acids may either accelerate or impede the sorption–desorption of PTEs. Organic acids have a significant impact on PTE mobilization/immobilization because they usually have functional groups like carboxyl and hydroxyl in their structures. These functional groups can interact with PTEs in soil and undergo a variety of processes, including as ion exchange and redox complexation, which can either stabilize or release PTEs (Araujo et al. 2019; Li et al. 2021). Researchers have used various adsorbents such as clay minerals, oxides, phyllosilicates, and organic adsorbents to reduce the bioavailability and increase immobilization of PTEs (Kumpiene et al. 2008; Komárek et al. 2013; Gao et al. 2019; Mazloomi and Jalali 2019). The use of nanoparticles as adsorbents has become common (Oloumi et al. 2018; Hughes et al. 2017; Guerrón et al. 2021). Nanoparticles have high efficiency in the adsorption of PTEs from aqueous and soil solutions (Sharma et al. 2009; Tang et al. 2014; Naderi Peikam and Jalali 2019). Nanoparticles such as aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2) have been shown to be efficient in removing PTEs from contaminated soil and solutions (Wang et al. 2009; Singh et al. 2011; Mahdavi et al. 2013, 2015) because of their large particle surface reactivity, huge porosity, great mechanical strength, temperature stability, and relatively reasonable price. Nanoparticles were also used in the soil column leaching procedure to lessen the leaching of PTEs from sandy soils with limited adsorption capabilities (Mohebian et al. 2022).

However, the effectiveness of the stabilization methods is often affected by a number of environmental factors. Plant root exudates contain active components known as low-molecular-weight organic acids (LMWOAs) (Perelomov et al. 2011; Onireti et al. 2017) and there were able to mobilize PTEs in contaminated soils (Rocha et al. 2015; Onireti et al. 2017). The adsorption of PTEs by nanoparticles can be affected by organic and inorganic ligands in water and soil. The adsorption of PTEs by soil using different adsorbents and the combination of the adsorbents with organic acids depends on the concentration and complexity of organic acid, the capacity, and sorting of PTEs in the solid and solution phases, and the characteristics of the adsorbent surface (Wang et al. 2009). The complexing agents can reduce or increase the adsorption of PTEs by soil (Zhang et al. 2021; Zhu et al. 2020). For example, the impact of different organic and inorganic ligands on the adsorption of PTEs by adsorbents showed that these compounds enhanced PTEs adsorption by kaolinite and goethite by creating triple surface-metal–ligand complexes, increasing the electrostatic potential of the surface and ligand–metal deposition (Stietiya and Wang 2011, 2014). Perelomov et al. (2011) by examining the adsorption of Cu and Pb by iron oxides with or without organic acids showed that by increasing the ligand to

PTEs ratio from zero to 10, the adsorption of both PTEs first increases and then decreases or remains constant and that the acid citric has a greater effect on PTE adsorption than oxalic and glutamic acid. Although the impact of organic acids on PTEs adsorption by clay minerals, Fe and Al oxides, and nanoparticles as well as soils treated with these adsorbents has been studied by researchers, however, studies in this field are limited (Komárek et al. 2013). Several types of research have been carried out to better understand the chemical mechanisms underlying the immobilization of PTEs by nanoparticle materials, with a focus on aqueous experiments. Although these experiments are useful, extending their applications to soils under vegetation may be limited due to a failure to consider the effect of LMWOAs in soils (Achor et al. 2020). They conducted experiments to examine the release of PTEs in the presence of both biochar and LMWOAs and indicated that mobilization of PTEs in biochar-amended soils depends on the interaction between the LMWOAs and the alkaline materials of the biochar. Typically, several PTEs are present in soils simultaneously and compete with one another for sorption sites. The availability and leaching of PTEs in soils are significantly impacted by the competitive sorption–desorption processes (Mohebian et al. 2022; Davari et al. 2015; Mahdavi et al. 2015; Jalali and Moradi 2013; Antoniadis et al. 2007). Consequently, it makes sense to investigate the adsorption–desorption of different PTEs in soils under competitive conditions. Some researchers have indicated how competitive sorption affects PTEs' sorption–desorption and leaching processes (Boostani et al. 2019; Joseph et al. 2020). Jiang et al. (2012) performed batch investigations to determine how pH and LMWOAs affected the competitive adsorption–desorption of Cd and Pb in Chinese paddy soils. According to Mohebian et al. (2022), leaching of PTEs from nanoparticle-modified sandy soil decreased under competitive systems for Cd, Cu, Co, Ni, and Zn. The competition between two or more PTEs in the presence of organic or inorganic ligands has not been extensively studied (Caporale and Violante 2016). Perelomov et al. (2011) looked at how the presence or absence of oxalate affected the adsorption of Cu and Pb on goethite. Competitive adsorption–desorption of PTEs in soils modified with nanoparticles using LMWOAs is still little studied. Thus, it is necessary to better understand the functions of nanoparticles in terms of PTEs immobilization in rhizospheric environments. There has been less systematic research to date into the effects of nanoparticles on PTE adsorption in the soil in the presence of organic acids in single and competitive systems. Thus, the current study sought to study the impact of two nanoparticles (Al_2O_3 and TiO_2) on the behavior of PTEs in vineyard soil when two common LMWOAs (citric and malic acids) were present in the single and competitive systems.

2 Materials and methods

2.1 Preparing the soil for adsorption tests

A sample of vineyard soil was used for adsorption isotherm experiments. To study the impact of nanoparticles on the adsorption of PTEs, nanoparticles including Al_2O_3 and TiO_2 were added to the soil at a rate of 2% by weighing and incubated for seven days at 25 °C and 75% of the field capacity. The samples were then dried and crushed and stored for subsequent experiments. Soil chemical and physical properties were measured using standard methods (Rowell 1994).

2.2 Nanoparticles and organic acids

Aluminum oxide and TiO_2 nanoparticles were prepared from Tekan and Nabvand companies with a purity of more than 99% and their properties were determined and reported by Mahdavi et al. (2013). Scanning electron microscope-energy dispersive X-ray (SEM–EDX) (Philips XL30 model) was used to obtain the morphological images of the surface of nanoparticles. The transmission electron microscopy (TEM) was used to determine the shape and dimensions of adsorbents. Using the Brunauer–Emmett–Teller (BET) equation, the specific surface area, total pore volume, and pore size distribution of materials were computed, and X-ray diffraction analysis (XRD) device (Seifert 300 model) was used to identify their crystals (Mahdavi et al. 2013). Citric acid and malic acid, which are the most abundant LMWOAs in the rhizosphere, were used to test the adsorption isotherms of PTEs. In all treatments in which organic acids were used, their concentrations were considered to be 10 mmol. In this study, two types of nanoparticles, as well as two types of organic acids, were used to compare their performance with each other and also with conditions without nanoparticles and organic acids.

2.3 Adsorption isotherms

Adsorption isotherms of Cd, Cu, Ni, and Zn were performed in closed conditions on soil samples treated with nanoparticles and untreated soil (control soil). In a single system, 25 ml of soil solution containing only one of the studied PTEs with initial concentrations of 0, 10, 25, 50, 100, 200, 400, and 600 mg l^{-1} was added to 2.5 g of soil. Their chloride salts (CdCl_2 , CuCl_2 , NiCl_2 , and ZnCl_2) were used to make solutions of PTEs. In the competitive system, 25 ml of a solution containing all PTEs was added to 2.5 g of soil so that each of the PTEs had the same initial concentration as the single system. To regulate the ionic strength of the solution, all added solutions contained 10 mmol sodium nitrate salt as the electrolyte. Sodium, especially

at low concentrations, has the least competition with PTEs for adsorption (Wei et al. 2014). In the treatments where the effect of organic acids was studied, in addition to PTEs and equilibrium solutions, 10 mmol of citric acid or malic acid was added. The prepared samples were stirred at room temperature for 1 h and left for 24 h and then shaken for another 1 h, and then centrifuged at 4000 rpm for 10 min. After this step, the samples were filtered using Whatman No. 42, and the concentration of PTEs in equilibrium solution was measured using an atomic absorption spectrophotometer. The amount of adsorbed PTEs in each sample was calculated using the following equation:

$$q_e = (C_i - C_e)/M \times V$$

where q_e is the amount of adsorbed PTEs (mg kg^{-1}), C_i and C_e are the initial and equilibrium concentrations of PTEs (mg l^{-1}), V is the volume of solution (ml), and M is the weight of the soil (kg). The adsorption of PTEs in different treatments was evaluated by fitting experimental data with the Freundlich equation. This equation was presented in the linear form:

$$\text{Ln}q_e = \text{Ln}K_F + 1/n \times \text{Ln}C_e$$

where K_F is the Freundlich distribution coefficient (l kg^{-1}) and n is the constant of the equation (without units), which indicates the tendency and intensity of adsorption of the adsorbent on the adsorbent.

2.4 Speciation of potentially toxic elements using MINTEQA2

The computer code MINTEQA2 was used to calculate the Cd, Cu, Ni, and Zn speciation over different pH in the single and competitive systems in the presence and absence of organic acids in solution in control soils (Allison et al. 1991). The calculations used the initial concentrations of Cd, Cu, Ni, and Zn, sodium nitrate concentrations, and initial concentrations of citric and malic acid, as well as a fixed carbon dioxide pressure of $10^{-3.5}$ atm. The content of calcium carbonate in soil was also considered in the calculation. The equilibrium pH for control soils was calculated by the model for single and competitive systems.

2.5 Quality control and statistical analysis

Quality assurance and control were used for analytical data, standard methods, and the careful monitoring of reagent blanks and standards. Calibrations and standards were used to calibrate the equipment and tools. To identify any sources of contamination, blank samples were used. The chemical reagents used in the experiment were all of the analytical grades. The experiment was conducted in two replicates. To

investigate the differences between treatments, the analysis of variance was used. The Duncan test was used to compare the means. All data were analyzed with SPSS 13.0, and graphs were created with EXCEL. The $P < 0.05$ was considered statistically significant.

3 Results and discussion

3.1 Characteristics of the studied soil in the presence and absence of nanoparticles

Table 1 displays the physical and chemical properties of the studied soil, as well as the soil spike with 2% nanoparticles. The soil is classified as Typic Xerorthents and has a light sandy loam texture. The pH of the soil was alkaline, and the contents of total Cd, Ni, and Zn were lower than the Beygi and Jalali (2018) background values, while the content of Cu was slightly higher than Cu background value. Properties such as pH, electrical conductivity (EC), and cation exchange capacity (CEC) changes as nanoparticles are added to the soil are presented in Table 1. The CEC of soil increased as a result of the addition of nanoparticles.

3.2 Properties of nanoparticles

The negative zeta potential of particles indicates that the charge of both nanoparticles is negative. The TEM analysis showed that the shape of Al_2O_3 and TiO_2 particles is circular and their size is 11 and 12 nm, respectively (Mahdavi et al. 2013). Due to the variability of grain size in TEM

pictures, the particle dimension indicated by TEM was either equal to or less than the matching crystallite size. Also, the specific area of Al_2O_3 ($105.8 \text{ m}^2 \text{ g}^{-1}$) is more than that of TiO_2 ($45.4 \text{ m}^2 \text{ g}^{-1}$), which indicates its greater ability of adsorption (Mahdavi et al. 2013). The SEM images showed smooth surfaces with high uniformity for the two particles. For Al_2O_3 and TiO_2 , the total pore volume was 0.380 and $0.253 \text{ cm}^3 \text{ g}^{-1}$, respectively, indicating that Al_2O_3 had a greater pore volume. Aluminum oxide mean pore size was smaller than that of TiO_2 (22.31 nm) (Mahdavi et al. 2013).

3.3 Potentially toxic elements adsorption in a single system

The single adsorption isotherms of Cd, Cu, Ni, and Zn in control soil and nanoparticle-treated soils in the presence and absence of organic acids are shown in Fig. 1. Changing the slope of the graphs with increasing equilibrium concentration indicates the existence of different adsorption sites with different energies (Wang et al. 2013). When organic acids were present, the adsorption of all PTEs was reduced. Vítková et al. (2015) showed that organic acids with different concentrations are present in the root zone of plants and therefore the efficiency of nanoparticles and oxides in immobilization and adsorption of PTEs in the soil is affected by organic acids. Organic acids have different negative charges with different solubility constants and number of different carboxyl groups. Organic acids with a carboxyl group have little complexing ability with PTEs, but ligands such as citrate, malate, and oxalate have greater ability to complex PTEs such as Fe and Al (Komárek et al. 2013).

Cadmium adsorption in all treatments (with and without organic acid) in TiO_2 -treated soil was higher than Al_2O_3 treated soil both in the presence and absence of organic acids. When organic acids were present, the amount of adsorption decreased and this decrease was greater in the presence of citric than malic acid (Fig. 1). The type and concentration of organic acid are effective in reducing or increasing the adsorption of PTEs in the soil (Wang et al. 2013). Huang et al. (2010) showed that the adsorption of Cd by adsorbents increases at low concentrations of organic acids (less than 1 mmol) but higher concentrations decrease adsorption. The adsorption isotherm of Cd in the presence of citric acid and Al_2O_3 treatment was different from other treatments so that up to the initial concentration of 100 mg l^{-1} the amount of adsorption was less than control treatment but increased in the final concentrations. This may be related to the non-adsorption of PTE-ligand complexes by Al_2O_3 nanoparticles, but as the ratio of PTE to ligand increases, the adsorption of PTE ions by nanoparticles increases.

The amount and percentage of increase in PTEs adsorption relative to the control soil at the last equilibrium concentration in Al_2O_3 - and TiO_2 -treated soils in a single system

Table 1 Some chemical and physical properties of the studied soil with and without nanoparticles

Properties	Unit	Soil	Al_2O_3 - treated soil	TiO_2 - treated soil
pH	-	7.9	7.7	7.6
EC	dS m^{-1}	0.22	0.27	0.29
CEC	$\text{cmol}_c \text{ kg}^{-1}$	14.7	15.6	15.0
CaCO_3	%	7.6	-	-
OM	g kg^{-1}	17.6	-	-
Clay	g kg^{-1}	161	-	-
Sand	g kg^{-1}	535	-	-
Silt	g kg^{-1}	305	-	-
Total potentially toxic elements				
Cd	mg kg^{-1}	1.2	-	-
Cu	mg kg^{-1}	32.1	-	-
Ni	mg kg^{-1}	34.2	-	-
Zn	mg kg^{-1}	48.2	-	-

EC electrical conductivity, CEC cation exchange capacity, CaCO_3 equivalent calcium carbonate OM organic matter

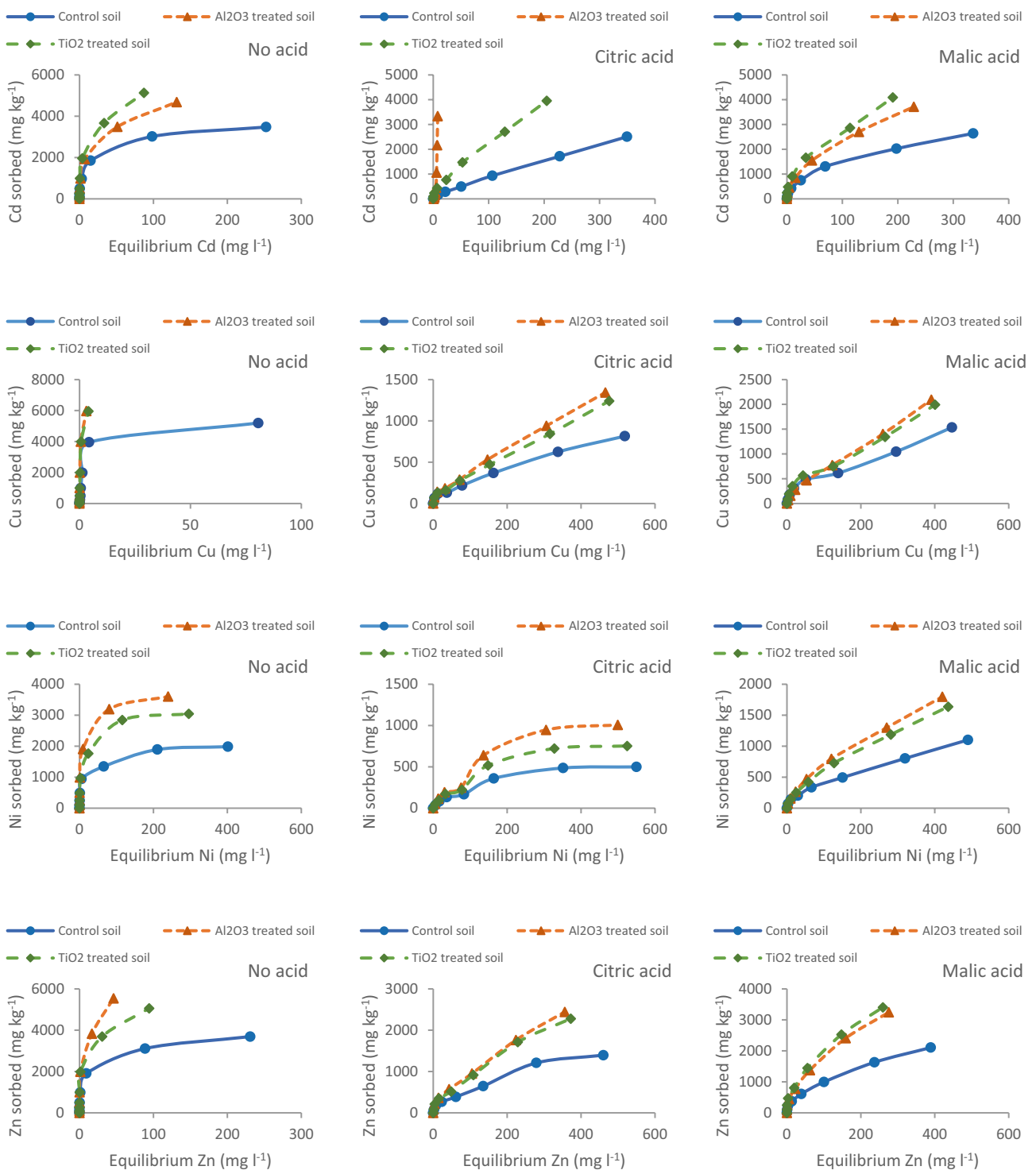


Fig. 1 Adsorption of potentially toxic elements in the absence and presence of organic acids in control and nanoparticle-treated soils in a single system

are shown in Table 2. The percentage of Cd adsorption in all treatments decreased with increasing equilibrium concentration. However, with increasing equilibrium concentration, the percentage of decrease in adsorption for nanoparticle soil was lower than control soil, and as a result, the highest percentage of increase in adsorption in nanoparticle treatments

compared to control soil was observed in the last equilibrium concentration. The percentage of increase in Cd adsorption in the treatment of TiO₂ nanoparticles in the presence of citric acid (57.8%) and both nanoparticles in the presence of malic acid (40.6% for Al₂O₃ and 54.9% for TiO₂) was higher than the control soil (Table 2). This indicates the greater effect of

nanoparticles on increasing the adsorption in the presence of organic acids, which can be due to the adsorption of organic acids on adsorbent surfaces and thus increase the negative surface charge or adsorption of complexes formed by them (Wang et al. 2009). Xu et al. (2003) showed the sequence of citric acid > malic > oxalic > acetic acid in increasing the negative charge of the surface. Wang et al. (2013) showed that with increasing the pH of the initial solution, the percentage of Cd adsorption in the soil increased.

Copper adsorption in all treatments, unlike Cd, had higher adsorption in Al₂O₃ treated soil than in TiO₂-treated soil in both organic acids. Adsorption was strong in the absence of organic acids, but sharply decreased in the presence of organic acids, and this decrease was greater in the presence of citric acid than malic acid (Fig. 1). Stronger bonding of organic acids with Cu than other PTEs ions causes a greater reduction in its adsorption (Wang et al. 2009). The amount of Cu adsorption in Al₂O₃ treatment and in the presence of malic acid up to the initial concentration of 100 mg l⁻¹ Cu was less than the control treatment but increased in the final concentrations. The percentage of adsorption of Cu in all treatments decreased with increasing equilibrium concentration and also the highest percentage of increase in adsorption in nanoparticle treatments compared to control soil was observed in the last equilibrium concentration (Table 2). The amount and percentage of increase in adsorption in nanoparticle treatments compared to the control soil in the treatment without organic acid were less than in the treatment with an organic acid. The highest amount of increase in adsorption was 775.1 and 765.8 mg kg⁻¹ which belonged to treatments without organic acids. The highest percentage of increase in adsorption was observed in Al₂O₃-treated soil in presence of citric acid (64.9%). Najafi and Jalali (2015) found that the effect of organic acids on Cu adsorption is greater than that of Cd, due to the greater stability constant of Cu complex.

Nickel adsorption, like Cu, was higher in all treatments in Al₂O₃ treated soils than in TiO₂-treated soils and was higher in both treatments than in control soils. Nickel adsorption was the lowest compared to other PTEs and its adsorption was reduced in the presence of organic acids (Fig. 1). The adsorption percentage of Ni, like Cu and Cd, decreased in all treatments with increasing equilibrium concentration, but in the presence of citric acid, the adsorption percentage of all treatments increased at 200 mg l⁻¹ of the initial solution and then decreased. The highest percentage of adsorption was observed in the nanoparticle treatments compared to the control soil at the last equilibrium concentration. The percentage of increase in Ni adsorption in different treatments had different patterns from other PTEs and only the percentage of increase in adsorption of Al₂O₃ treatment compared to the control soil in the presence of citric acid was 101.8% higher than in the case without organic acid. The highest and lowest percentage of increase in Ni adsorption belonged to Al₂O₃ treatment in presence of citric acid and TiO₂ treatment with malic acid, respectively (Table 2). This indicates that the presence of malic acid with TiO₂ nanoparticles reduces the effect of these adsorbents on the adsorption of Ni in the soil.

Zinc adsorption in soil with no organic acids and the presence of citric acid in Al₂O₃-treated soils was higher than in TiO₂-treated soils, but in the presence of malic acid, as in Cd, adsorption was higher in TiO₂-treated soils. This indicates that malic acid is more effective in absorbing Zn by TiO₂. Zinc adsorption, like Cu, was very high in the absence of organic acids, but unlike Cu, organic acids had less effect on reducing its adsorption. However, the decrease in adsorption in the presence of citric acid was greater than that of malic acid (Fig. 1). The greater effect of citric acid on the adsorption of Zn can also be attributed to its greater acidity. The percentage of Zn adsorption, like Cd, Cu, and Ni, decreased in all treatments with increasing equilibrium

Table 2 Amount and percentage of increase in potentially toxic elements adsorption in nanoparticle-treated soils compared to control soil (mg kg⁻¹) at the last equilibrium concentration in the single system

Organic acids	Treatment	Cd		Cu		Ni		Zn	
		Control	Increase	Control	Increase	Control	Increase	Control	Increase
No organic acid	Al ₂ O ₃ -treated soil	3475.5	1209.7 (34.8)	5194.0	775.1 (14.9)	1984.3	1620.3 (81.7)	3691.2	1849 (50.1)
	TiO ₂ -treated soil		1654.2 (47.60)		765.8 (14.7)		1060.3 (53.4)		1367.3 (37.0)
Citric acid	Al ₂ O ₃ -treated soil	2505.6	831.9 (33.2)	815.2	528.7 (64.9)	499.6	508.4 (101.8)	1395.5	1047.1 (75.0)
	TiO ₂ -treated soil		1447.7 (57.8)		425.7 (52.2)		253.2 (50.7)		823 (63.3)
Malic acid	Al ₂ O ₃ -treated soil	2640.2	1072.3 (40.6)	1535.7	557.6 (36.3)	1101.8	695.7 (63.1)	2107.4	1136.6 (54)
	TiO ₂ -treated soil		1450.5 (54.9)		457.2 (29.8)		535.7 (48.6)		1297.6 (61.6)

concentration. Also, the highest percentage of increase in adsorption was observed in the treatments with nanoparticles compared to the control soil at the last equilibrium concentration. Aluminum oxide and TiO₂-treated soils in the presence of citric acid with 75.0% and 63.3% had the highest increase in percentage of Zn adsorption, respectively (Table 2). It should be noted that in all PTEs, the percentage of increase in adsorption in citric acid was often higher, indicating a greater effect of this organic acid in reducing the mobility of PTEs, likely due to that it promotes the formation of triple bonds with absorbent surfaces or precipitation of PTE complexes. Tan et al. (2007) by examining the adsorption of thorium by TiO₂ nanoparticles under different conditions in the presence of humic and fulvic acids showed that these two organic compounds increase the adsorption by nanoparticles and it was also found that the surface complex is the main mechanism in adsorption.

3.4 Potentially toxic elements adsorption isotherms in the competitive system

Competitive adsorption isotherms of Cd, Cu, Ni, and Zn in control soil and nanoparticle-treated soils in the presence and absence of organic acids are shown in Fig. 2. The different behaviors of varying treatments in the competitive adsorption of PTEs are related to the nature of adsorption sites, adsorption mechanisms, and finally to the properties of the PTEs (Serrano et al. 2009; Davari et al. 2015). At low concentrations of PTEs, due to the presence of more adsorption sites, competition between PTEs is less, but with increasing concentrations of PTEs and decreasing adsorption capacity, competition increases, and PTEs such as Ni, which have low competitiveness, is removed from adsorption sites by other PTEs with strong binding affinity. Mahdavi et al. (2012) by examining the adsorption of Cd, Cu, Ni, and Pb on Fe₃O₄, ZnO, and CuO nanoparticles showed that the adsorption was less in the competitive system than in the non-competitive system. In the absence of organic acid in the system, the highest amount of adsorption in all treatments belonged to Cu and the adsorption isotherms of Cd and Zn were similar, followed by Ni. Under these conditions, with the presence of nanoparticles, the adsorption of all PTEs increased and the addition of Al₂O₃ and TiO₂ to the soil caused a greater increase in the adsorption of Ni and Cd, respectively (Fig. 2). The reason for the higher adsorption of Cu is the high tendency of this PTE to specific adsorption in soil. Atanassova (1995) showed that in the competitive PTE adsorption system, the increase in Cu adsorption is associated with a decrease in the adsorption of Cd, Ni, and Zn. Davari et al. (2015) examined the competitive adsorption of Cd and Ni and found that both PTEs compete for similar sites and the effect of Cd on Ni adsorption was greater.

In the presence of citric acid, the adsorption of all PTEs decreased but only the reduction in adsorption of Cu was so great that it caused the adsorption of Cd to be the highest in these conditions and the adsorption of Zn was higher than Cu except in the last equilibrium concentration. This indicates a greater effect of citric acid on Cu adsorption in the competitive system compared to other PTEs. Cadmium adsorption, like the single system, was lower than the control treatment up to an initial concentration of 100 mg l⁻¹ in the presence of citric acid and the Al₂O₃ treatment and then increased. In the presence of TiO₂ nanoparticles, due to the greater effect of this adsorbent on Cd adsorption, Cd had the highest adsorption. This can be attributed to the existence of specific sites for the adsorption of Cd in these nanoparticles.

As in a single system, the adsorption percentage of all PTEs in all treatments decreased with increasing equilibrium concentration, which indicates the saturation of specific adsorption sites with increasing PTE concentration. However, in some treatments, the percentage of adsorption did not decrease, and in the final equilibrium concentrations, an increase in the percentage of adsorption was observed. The highest increase in the percentage of adsorption of Cd (82.2%) was observed in TiO₂-treated soil without organic acids, while the highest increase in the percentage of adsorption of Cu (65.2%), Ni (67.9%), and Zn (65.0%) was observed in Al₂O₃-treated soil in presence of citric acid (Table 3). The greater tendency of one PTE than another to adsorb can be attributed to the properties of ions such as atomic weight, ionic radii, electronegative, hydrolysis constant, and softness parameter (Usman 2008). Non-hydrated and constant radii of hydrolysis further result in stronger electrostatic adsorption of the PTE (Antoniadis et al. 2007). Stietiya and Wang (2014) examining the competitive adsorption isotherm of Cd and Zn and indicated that Zn has a higher tendency than Cd to adsorb by Al₂O₃ nanoparticles and citrate ligand only reduced the adsorption of Zn to about 25% in the single system but in other cases increased adsorption. The increase in adsorption was due to the formation of tridentate ligand or deposition of PTE-ligand complex and the decrease in adsorption was reported due to the low tendency of organic acid to adsorb or form a strong complex with PTE ions.

3.5 Parameters of PTE adsorption isotherms in the single and competitive systems

The parameters of PTE adsorption in the single system for the Freundlich equation are shown in Table 4. Linear and Langmuir equations were also fitted, but the Freundlich equation for all PTEs and treatments had a good fit to the data and had a high coefficient of determination and a low standard error percentage. Mahdavi et al. (2013) showed

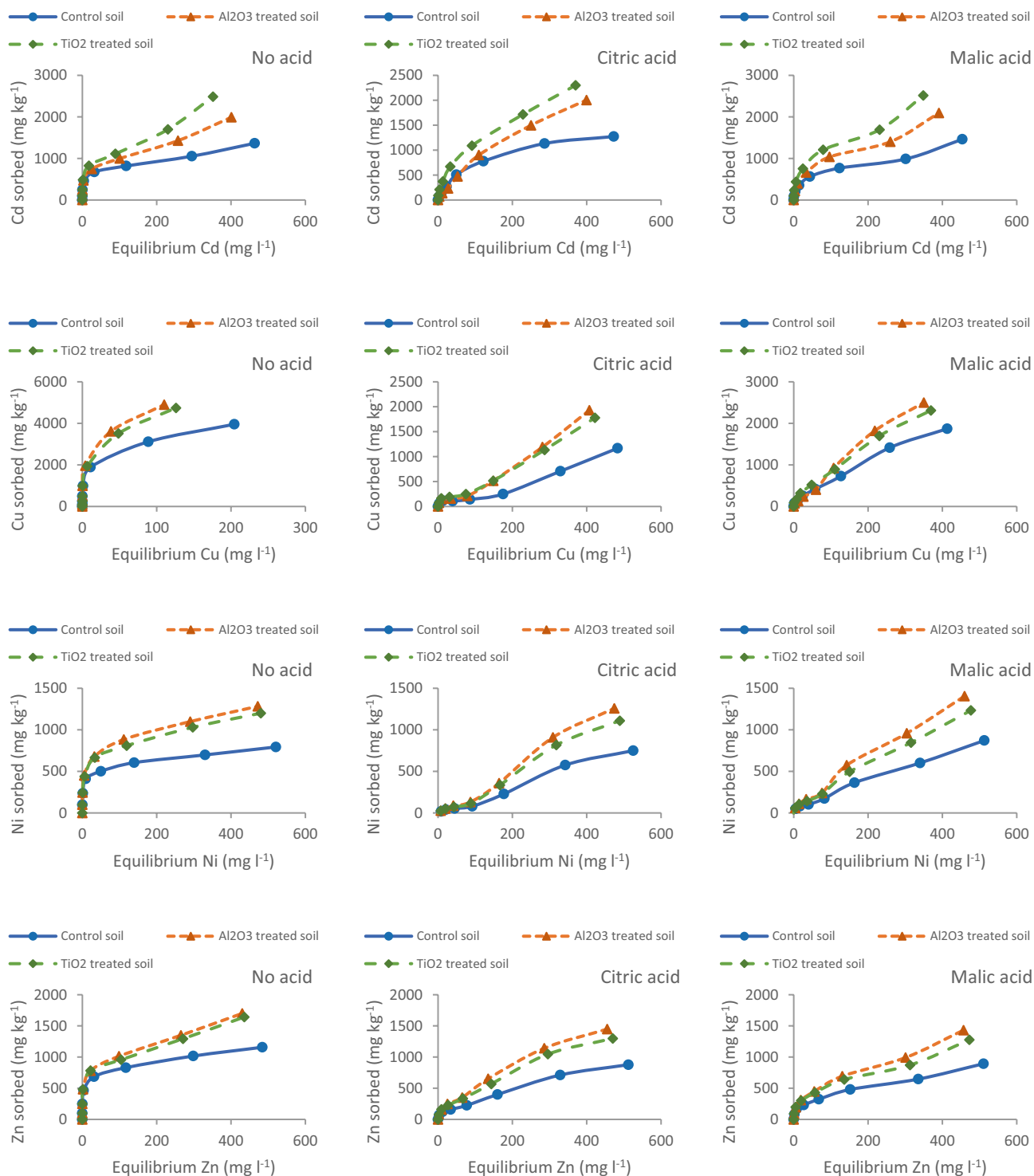


Fig. 2 Adsorption of potentially toxic elements in the absence and presence of organic acids in control and nanoparticle-treated soils in the competitive system

that the Freundlich equation in both single and competitive systems describe the adsorption of Cd, Cu, and Ni by nanoparticles better than the Langmuir equation.

The value of parameter n was between 1 and 10, which confirmed the goodness fit of this equation. The value of

the Freundlich distribution coefficient was well indicative of adsorption changes in different treatments. As a result, the values in the treatments with nanoparticles were higher than in the control soil, and the values without organic acid were higher than in the treatments with

Table 3 Amount and percentage of increase in potentially toxic elements adsorption in nanoparticle-treated soil compared to control soil (mg kg⁻¹) at the last equilibrium concentration in the competitive system

Organic acids	Treatment	Cd		Cu		Ni		Zn	
		Control	Increase	Control	Increase	Control	Increase	Control	Increase
No organic acid	Al ₂ O ₃ -treated soil	1364.6	626.3 (45.9)	3956	944.20 (23.9)	59.793	489.0 (61.6)	1157.4	542.6 (46.9)
	TiO ₂ -treated soil		1121.9 (82.2)		749 (19.8)		406.4 (51.2)		485.1 (42)
Citric acid	Al ₂ O ₃ -treated soil	1272.9	732.1 (55.7)	1168.0	761.2 (65.2)	50.749	508.6 (67.9)	877.7	570.8 (65.0)
	TiO ₂ -treated soil		1027.1 (80.7)		611.0 (52.3)		360.2 (48.1)		420.8 (48)
Malic acid	Al ₂ O ₃ -treated soil	1462.6	631.2 (43.2)	1870	630 (33.7)	81.871	533.4 (61.2)	893.2	538.4 (60.3)
	TiO ₂ -treated soil		1542.2 (72)		439.4 (23.5)		361.9 (41.5)		383.1 (42.9)

organic acids. In the absence of organic acids, as well as in single and competitive systems, the addition of nanoparticles increased the K_F of all PTEs (Tables 4 and 5), with Cu having a higher K_F in both systems. In all treatments, the K_F values of PTEs were much lower in the presence of citric and malic acid than in the absence of organic acid, and this reduction was more pronounced in the presence of citric acid than in the absence of malic acid (Tables 4 and 5). Based on K_F values, Cd had higher adsorption in TiO₂-treated soils in the presence of both citric and malic acids, particularly malic acid, whereas other PTEs differed in different treatments in both systems. This suggests that Cd may be more stable in the presence of organic acids and TiO₂ nanoparticles, posing less of an ecotoxicological threat. Organic acids can complex with PTEs, increasing the release of PTEs that is adsorbed in soils as surface complexes and precipitates (Xu et al. 2019; Hahladakis et al. 2014).

In both systems, the K_F value of Cu in the presence of malic acid was higher in TiO₂-treated soils than Al₂O₃-treated soils (Tables 4 and 5). The K_F values of Ni in the presence of malic and citric acid were higher in Al₂O₃-treated soils than in TiO₂-treated soils, as in both single and competitive systems. The trend of K_F values for Zn differed from that of other PTEs. In the presence of citric acid and in both single and competitive systems (Tables 4 and 5), the K_F values of Zn were higher in Al₂O₃-treated soils than in TiO₂ treated soil, whereas in the presence of malic acid and in both single and competitive systems, the K_F value in Al₂O₃-treated soil was lower than TiO₂-treated soil. This means that the type of organic acid, as well as the type of nanoparticles and PTEs, influences the decrease or increase in K_F values. Jalali and Moradi (2013) by examining the competitive adsorption of PTEs in calcareous soils of Hamadan province showed that the lowest adsorption belonged to manganese and Ni which indicates more mobility of these two PTEs in the soils.

The sequence of PTEs adsorption based on K_F values in both single and competitive systems is shown in Table 6. The K_F sequence in control soil and in the absence of organic acids in the single system was Zn > Cu > Cd > Ni, while in the competitive system, Cu replaced Zn in the above sequence. In the presence of Al₂O₃ and TiO₂ nanoparticles and in single and competitive systems, the sequence was Cu > Zn > Cd > Ni (Table 6). The K_F sequence in control soil and the presence of citric acid in the single system was Zn > Cd > Cu > Ni, while in the competitive system, Cd replaced Zn in the above sequence. In the presence of Al₂O₃ nanoparticles and in single system, the sequence was Zn > Cu > Ni > Cd while in the competitive system, Cd replaced Ni in this sequence, and in TiO₂-treated soil and in both single and competitive systems, the sequence was Cd > Zn > Cu > Ni (Table 6). The dominant K_F sequence in control and soils treated with nanoparticles in both single and competitive systems was Cd > Zn > Cu > Ni and only Ni replaced Cu in the Al₂O₃-treated soil. The results indicated that in presence of both organic acids, Cd and Zn had a higher affinity to being adsorbed in nanoparticles-treated soils. This could be due to the competition of Cd and Zn for adsorption on specific sites. Mahdavi et al. (2015) by examining the effect of Al₂O₃ and ZnO nanoparticles in reducing the bioavailability of PTEs in soil showed that in the non-competitive system, the adsorption sequence was Ni > Cd > Cu and in the competitive system was Cu > Cd > Ni. The adsorption sequence can also indicate the tendency of different organic acids to form a complex and ultimately affect adsorption.

Figure 3 depicts the effect of organic acids on the K_F values of PTEs by displaying the average K_F values of all treatments. As can be seen, the addition of organic acids, particularly citric acid, significantly reduced K_F values of

Table 4 Parameters of Freundlich equation fitted to the potentially toxic elements isotherm in different treatments in single system

Potentially toxic elements	Parameters	No organic acid			Citric acid			Malic acid		
		Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil	Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil	Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil
Cd	K _F (1 kg ⁻¹)	535	824.5	1259.3	29.9	15.5	151.4	137.9	247.5	448.0
	<i>n</i>	2.5	2.6	3.2	0.41	1.1	1.7	1.9	2.1	2.6
	<i>R</i> ²	0.96	0.98	0.98	0.99	0.98	0.99	0.99	0.99	0.99
	SE (%)	29.7	21.1	21.3	6.7	22	13.2	10.2	6	16.4
Cu	K _F (1 kg ⁻¹)	858.3	4280	3519.6	29.4	35.6	32.4	54.5	33.0	64.4
	<i>n</i>	1.7	1.7	1.5	2	1.8	1.8	1.9	1.5	1.8
	<i>R</i> ²	0.82	0.91	0.9	0.96	0.96	0.95	0.98	0.99	0.98
	SE (%)	70.9	53.9	100	21	21.7	23.6	15.0	6.8	17.0
Ni	K _F (1 kg ⁻¹)	320.4	637.9	460.08	14.3	19.7	18.0	36.9	40.5	38.6
	<i>n</i>	3	2.6	2.6	1.7	1.5	1.6	1.9	1.6	1.7
	<i>R</i> ²	0.89	0.92	0.95	0.98	0.97	0.98	0.99	0.99	0.99
	SE (%)	43.5	40.2	33.0	15	19.1	15.2	7.5	4.4	7.6
Zn	K _F (1 kg ⁻¹)	884.0	1884.1	1600.4	53.4	88.7	76.2	121	242.4	364.9
	<i>n</i>	3.6	3.7	4	2	1.8	1.8	2.1	2.3	2.8
	<i>R</i> ²	0.98	0.99	0.97	0.99	0.98	0.98	0.99	0.98	0.95
	SE (%)	58.5	70.8	71.2	12.5	15.4	17.3	8.3	43.4	45.6

Table 5 Parameters of Freundlich equation fitted to the potentially toxic elements isotherm in different treatments in competitive system

Potentially toxic elements	Parameters	No organic acid			Citric acid			Malic acid		
		Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil	Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil	Control	Al ₂ O ₃ -treated soil	TiO ₂ -treated soil
Cd	K _F (l kg ⁻¹)	255.0	313.7	416.6	41.2	25.6	101.7	106.6	123	211.2
	<i>n</i>	3.7	3.5	3.8	1.7	1.4	2	2.4	2.2	2.5
	R ²	0.97	0.99	0.98	0.98	0.99	0.99	0.99	0.99	0.99
	SE (%)	15.0	11.7	15	13.4	13	3.2	10.0	9.2	6.8
Cu	K _F (l kg ⁻¹)	806.4	1243.8	1074.6	22.1	30.4	38.1	41.2	25.5	74
	<i>n</i>	3.2	3.3	3.17	2	1.7	1.8	1.7	1.3	1.8
	R ²	0.97	0.95	0.98	0.81	0.86	0.90	0.98	0.86	0.64
	SE (%)	85.7	47.8	43.1	51	53.5	40.3	17.4	27.5	22.3
Ni	K _F (l kg ⁻¹)	199.7	305.6	279.8	2.2	3.1	3	13.3	19.0	18.4
	<i>n</i>	4.35	4.4	4.3	1.1	1.1	1.1	1.6	1.5	1.5
	R ²	0.97	0.99	0.99	0.96	0.96	0.98	0.96	0.97	0.96
	SE (%)	12.5	41	41	32.5	31	33.4	23.1	23.4	22.9
Zn	K _F (l kg ⁻¹)	344	475.2	469.8	33.1	50.1	46.1	65.5	87.8	99.2
	<i>n</i>	5.2	5.4	5.6	2	2	2	2.5	2.3	2.6
	R ²	0.99	0.99	0.97	0.96	0.98	0.98	0.99	0.99	0.99
	SE (%)	41	42	41.9	18.7	16.2	14.8	8.1	7.9	8.8

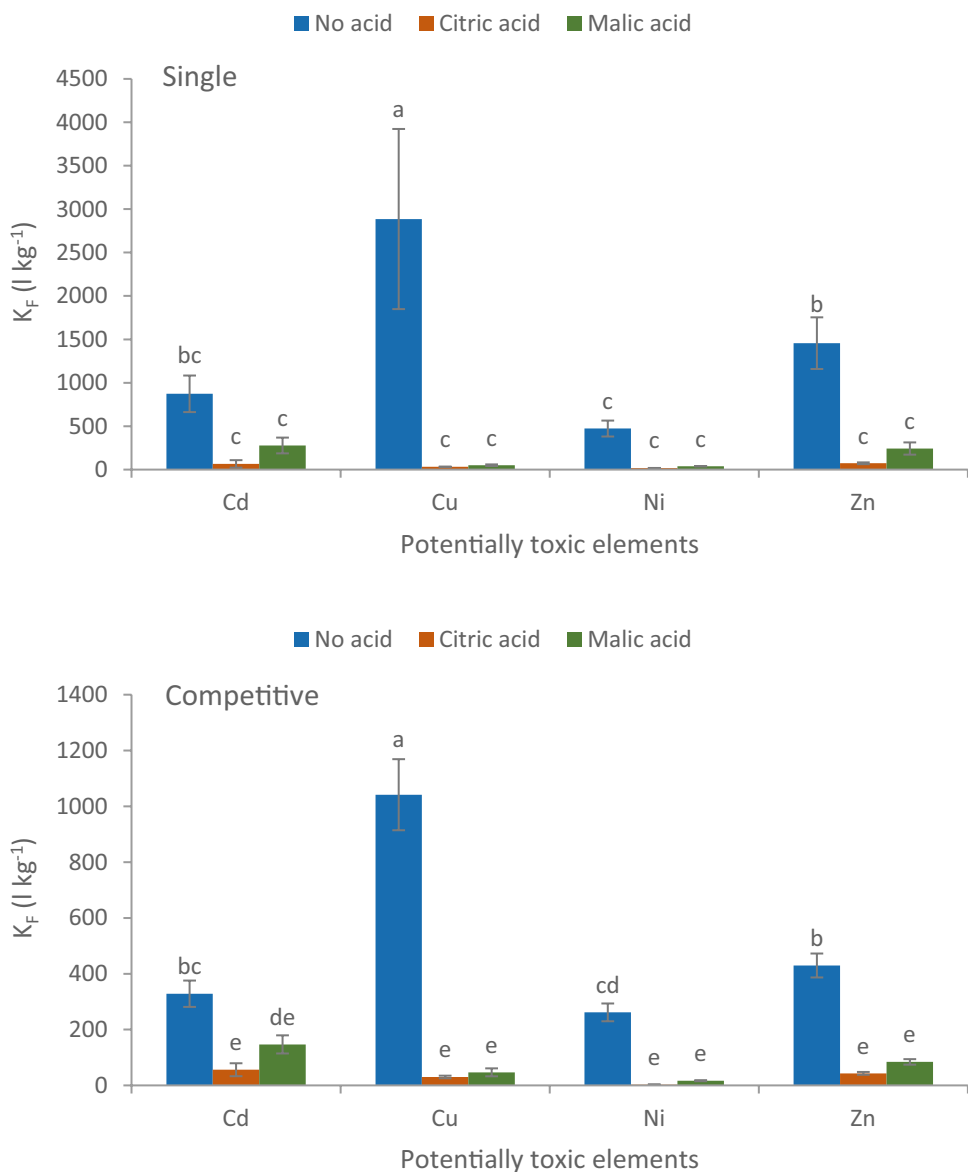
Table 6 The sequence of potentially toxic elements based on Freundlich adsorption coefficients in different treatments in single and competitive systems

Organic acids	Treatments	Single system	Competitive system
No organic acids	Control	Zn > Cu > Cd > Ni	Cu > Zn > Cd > Ni
	Al ₂ O ₃ -treated soil	Cu > Zn > Cd > Ni	Cu > Zn > Cd > Ni
	TiO ₂ -treated soil	Cu > Zn > Cd > Ni	Cu > Zn > Cd > Ni
Citric acid	Control	Zn > Cd > Cu > Ni	Cd > Zn > Cu > Ni
	Al ₂ O ₃ -treated soil	Zn > Cu > Ni > Cd	Zn > Cu > Cd > Ni
	TiO ₂ -treated soil	Cd > Zn > Cu > Ni	Cd > Zn > Cu > Ni
Malic acid	Control	Cd > Zn > Cu > Ni	Cd > Zn > Cu > Ni
	Al ₂ O ₃ -treated soil	Cd > Zn > Ni > Cu	Cd > Zn > Cu > Ni
	TiO ₂ -treated soil	Cd > Zn > Cu > Ni	Cd > Zn > Cu > Ni

Cd, Cu, and Zn in both single and competitive systems, while it also reduced K_F values of Ni, but not significantly in the single system. Some researchers have reported that citrate acid has a high performance in the remediation of

contaminated soils (Jean et al. 2012; Yang et al. 2020). Yang et al. (2020) indicated that among applied organic acids to improve the remediation of contaminated soils, citrate had the best performance.

Fig. 3 Mean Freundlich distribution coefficient of potentially toxic elements (control and nanoparticle-treated soils) in absence and presence of organic acids in single and competitive systems. Mean having different letter(s) among PTEs and treatments are statistically different at $P < 0.05$ according to Duncan’s test



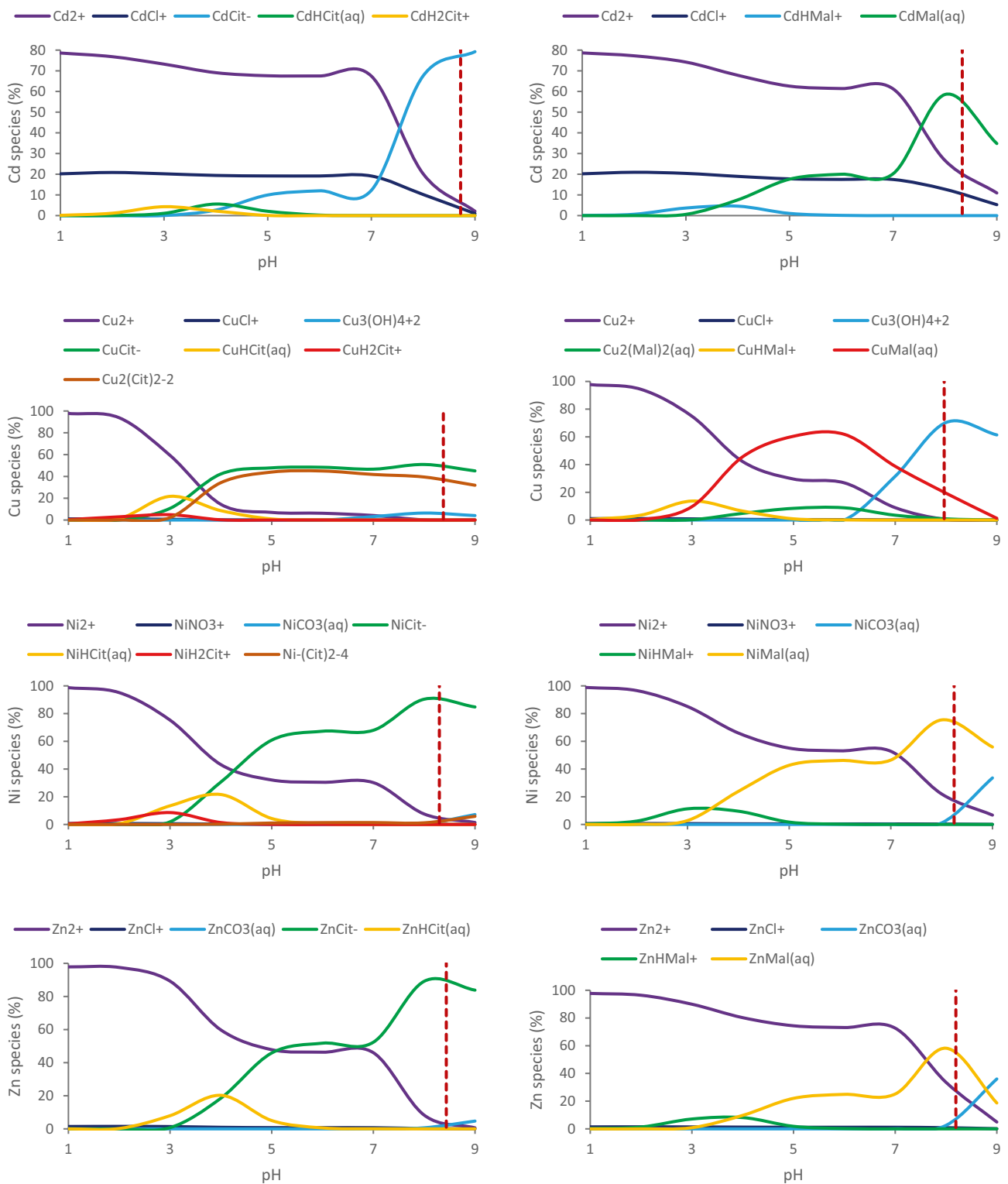


Fig. 4 Speciation of potentially toxic elements at last initial concentration (600 mg l^{-1}) in control soil in presence of organic acids in a single system. Dashed vertical lines indicate equilibrium pH in soil

3.6 Potentially toxic element speciation

Figures 4 and 5 show the results of PTE speciation in control soils in the presence of citric and malic acids in the

last initial concentration (600 mg l^{-1}) in the single and competitive systems. The following were the most common PTE species across the pH range in the presence of citric acid in the single system: Cd: Cd^{2+} , CdCl^+ , CdCit^- ;

Cu:Cu²⁺, CuCit⁻, CuHCit(aq), Cu₂Cit₂²⁻, Ni:Ni²⁺, Ni-Cit⁻, NiHCit(aq), NiH₂Cit⁺; Zn:Zn²⁺, ZnCit⁻, ZnHCit(aq), while the dominate species of PTEs in presence of malic acid for

species not to bind with malic was the same as citric acid, but PTEs bonded with malate were different and that the percentage of free PTEs was higher than citric acid (Fig. 4).

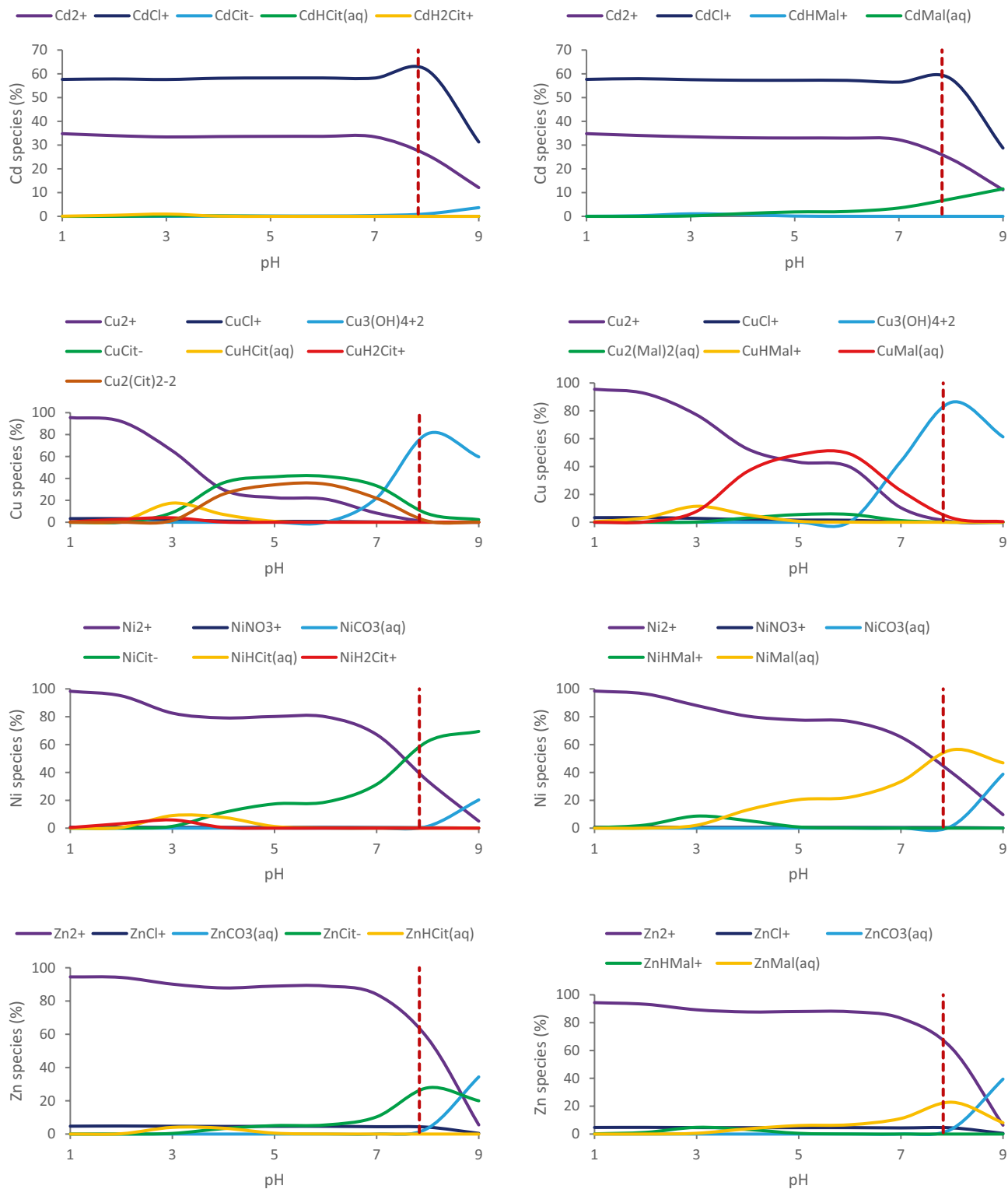


Fig. 5 Speciation of potentially toxic elements at last initial concentration (600 mg l^{-1}) in control soil in presence of organic acids in the competitive system. Dashed vertical lines indicate equilibrium pH in soil

The pH of the suspension at equilibrium with citric acid and malic acid for different PTEs in the single system was in the range of 8.3 to 8.7 and 8.0 to 8.4, respectively, indicating that CdCit^- , CuCit^- , $\text{Cu}_2\text{Cit}_2^{2-}$, NiCit^- , and ZnCit^- are dominant in the solution in presence of citric acid. On the other hand, in the presence of malic acid $\text{CdMal}(\text{aq})$, Cd^{2+} , CdCl^+ , $\text{Cu}_3(\text{OH})_4^{2+}$, $\text{CuMal}(\text{aq})$, $\text{NiMal}(\text{aq})$, Ni^{2+} , $\text{ZnMal}(\text{aq})$, and Zn^{2+} are dominant species, resulting in desorption and low adsorption of Cd, Ni, Zn, and Cu from the soils in citric acid medium. As indicated in the presence of malic acid, negative species were not present resulting in greater adsorption of PTEs. This confirms the finding stating that citrate, as a ternary acid, has a higher extraction ability for PTEs than acetate (unary acid) and oxalate and malate (binary acid), owing to more hydroxyl and carboxyl groups for complexing (An et al. 2011). In the competitive system and presence of citric and malic acid and across all pH, free Cd^{2+} was decreased, while Ni^{2+} and Zn^{2+} increased and Cu^{2+} was changed slightly (Fig. 5). On the other hand, the pH of the suspension at equilibrium with citric acid and malic acid for different PTEs in the competitive system was 7.8 and the dominant Cd species at this pH were changed from CdCit^- and $\text{CdMal}(\text{aq})$ (in single system) to CdCl^+ and Cd^{2+} species; the dominant Cu species was $\text{Cu}_3(\text{OH})_4^{2+}$ in both citric and malic acids; the dominant Ni species were NiCit^- and $\text{NiMal}(\text{aq})$; and the dominant Zn species was Zn^{2+} in both citric and malic acids (Fig. 5). In other initial concentration, the trend was approximately the same, but the percentage of species were different (Figures were not shown).

Poulsen and Hansen (2000) showed that the citrate ligand inhibits the adsorption of Ni due to the formation of the NiCit -complex. They indicated that citric acid ligands include NiH_2Cit^+ , NiHCit^0 , and NiCit^- according to the pH of the environment and that the negatively charged Ni-citrate complex (NiCit^-) was the dominant species at pH 6. Flynn and Catalano (2017) investigated the effect of oxalic acid on the adsorption of Ni by iron oxides and their results showed that by adding oxalic acid to the system, Ni adsorption is reduced due to the formation of the Ni-oxalate complex. They stated that the oxalate anion causes the type and tendency of Ni adsorption to change into triple surface-ligand-PET surface complexes.

Our findings have implications for optimizing remediation methods using nanoparticles as a soil amendment for reducing PTEs release from contaminated soils in presence of citric and malic acids. It is critical to comprehend the nature and composition of LMWOAs and their interactions with nanoparticles and PTEs. Because PTEs behave differently in LMWOA-nanoparticles systems, it is important to determine the dominant PTE types in the contaminated soils (Achor et al. 2020).

4 Conclusion

The adsorption of PTEs by nanoparticles can be affected by organic acids in soil. This study showed that the fate of PTEs can be influenced to varying degrees by the presence of other PTEs, the type of organic acids, and stabilizers in the soil environment. We conclude that the application of both nanoparticles to a calcareous soil at the studied rate increased the adsorption of Cd, Cu, Ni, and Zn and thus might immobilize those PTEs and decrease their mobility. It was also indicated that the efficiency of nanoparticles in immobilization and adsorption of PTEs in the soil is affected by organic acids. In the absence of organic acids, and the single and competitive systems and in all treatments, Cu was more strongly adsorbed, while Ni was the least adsorbed PTEs. When organic acid was present, the amount of adsorption decreased and this decrease was greater in the presence of citric acid than malic acid, which indicated the higher acidity and complexity of citric acid. The Cu experiences the highest decrease in both systems which is important in soils having multi-PTEs. The results indicated that the decrease or increase in Freundlich distribution values is determined not only by the type of organic acid but also by the type of nanoparticles and PTEs. Thus, determining the nature and composition of LMWOAs and the dominant PTEs, as well as their interactions with nanoparticles, is critical for better management in the remediation of PTE-contaminated soil.

Author contribution Mohsen Beygi: methodology, software, formal analysis, writing—review and editing, visualization. Mohsen Jalali: conceptualization, formal analysis, investigation, resources, data curation, writing—original draft, supervision, project administration. Jianxu Wang: formal analysis, data curation, writing—review and editing, visualization.

Availability of data and material Data can be available from the corresponding author upon request.

Declarations

Conflict of interest The authors declare no competing interests.

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