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Evaluating the Removal Efficiency of Potentially Toxic Elements (PTEs) from a Shale Deposit by Citric Acid

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THE MAJORITY of arable lands of Egypt are deserts, mainly sandy soils of low fertility, low water retention and high water and wind erodibility. Shale deposits (rich in clay minerals) might be considered suitable conditioners to improve soil physical, chemical and mineralogical properties and hence increase its productivity. However, these additives should not be a source of contaminants such as PTEs. Accordingly, a technical shale deposit sample was collected fromAbu Thor (longitudes between 33° 22″ and 33° 23″ E and latitudes between 29° 00″ and 29° 02″ N), Southwest Sinai. In this shale deposit sample, silica comprised 37.35% and alumina was about 18.37%. This sample also contained630 mg Mn, 7704 mg Zn, 19200 mg Fe, 2627 mg Pb, 2763 mg Co and 1310 mg Ni per kg. These levels are not environmentally acceptable in shale deposits when used for soil conditioning. Accordingly, removal or at least reduction in contents of these contaminants in shale deposits should be considered prior to their addition as conditioners to low fertile which exhibit low water holding soils such as the sandy ones. To attain this aim, PVC columns (6.8cm inner diameter× 45cm height) were filled with the shale deposit, washed with citric acid (conc: 10 g L^{-1}) at a flow rate of 1 mL per min. with a total volume of 3200 mL per column and the leachate was collected every 100 min to determine its content of PTEs. Cumulative extracted PTEs were calculated versus time and best fitted to the power function kinetic model. This extraction followed the sequence of Ni>Fe>Co>Pb≈Zn>Mn and, in general, the removal efficiencies were low and did not exceed 12% of Ni, 4% of Co, 2.97% of Mn, 2% of Pb and 1% for each of Fe and Zn. It can; therefore, be deduced that citric acid can only chelate the easily bounded forms of PTEs. More researches are needed to investigate the efficiency of citric acid for in-situ long term facilitated phytoextraction of PTEs from shale deposits to attain more acceptable levels

Keywords: potentially toxic elements; citric acid; removal efficiency; extraction; desorption kinetics.

1. Introduction

The majority of arable lands of Egypt are deserts, mainly sandy soils (Selim and Mosa, 2012) of high infiltration rate (Mahmoud, 2014), low water and nutrient holding capacities (Selim *et al*. 2009; Ghazi *et al.*, 2022). These soils are of low clay and organic matter contents (Minhal *et al*., 2020). To maximize their productivity, natural safe additives are guaranteed (Ali-Bik *et al*., 2022) such as clay (Minhal *et al*., 2020) and organic amendments (Abdelhafez *et al*., 2018; Elshony et al., 2019; Tolba *et al*., 2021; Farid *et al*., 2022).

Shale deposits, rich in clay minerals (Wilson and Wilson, 2014), can be used successfully to improve the characteristics of sandy soils (Eldardiry and Abd El-Hady, 2012; Hassan *et al*., 2016); yet contaminant founds in these shales should be lessened, prior to their use, to meet the acceptable environmental levels (Khurramovna *et al*., 2021). Potentially toxic elements are of special concern because these contaminants do not undergo biodegradation (Hashim *et al*., 2017; Abbas and Bassouny, 2018; Farid *et al*., 2019); hence possessing long term negative environmental impacts (Abdelhafez *et al*., 2015; Elshazly et al., 2019; Abdelhafez *et al*., 2021; Sarhan *et al*., 2021; Abd-El-Hady and Abdelaty, 2022; Asaad *et al*., 2022; Hussein *et al*., 2022; El-Shwarby *et al*., 2022; Mekawi *et al*., 2023).

Removing these contaminants via with H_2SO_4leaching may effectively lessen their content

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by more than 90% (Abdel-Wahab *et al*., 2017); yet, this process may have negative consequences on the quality of ground water (Nouri *et al*., 2008; Hashim *et al*., 2011). Organic acids such as citric acid has also high ability to extract potentially toxic elements in contaminated soils (Ding *et al*., 2014; Ash *et al*., 2016) while record a bit lower leaching efficiency versus mineral acids (Schwab *et al*., 2008). The advantages of using citric acid with soils is that this acid has little effect on the leaching soil macro-nutrients; while improve soil structure (Wasay *et al*., 2001). In facilitated phytoextraction, citric acid can be used to increase the removal efficiency of Cd, Cu and Pb from soils without increasing the risk of leaching (Kim and Lee, 2009). A point to note is that citric acid is an intermediate byproduct of some soil biota (Hu *et al*., 2019), which is characterized by its low molecular mass (Ash *et al*., 2016), high solubility in water and being easily biodegradable (Angumeenal and Venkappayya, 2013).

In an study made by Park *et al*. (2013), application of citric acid (2 kmole m^{-3} (≈384.24 g L^{-1}) to a PTEs contaminated soil reduced successfully the concentrations of Cu, Zn and by 86.5, 88.9 and 83.3%, respectively within only 120 min. Although, these results were promising; yet this high dose of citric acid may lead to negative environmental consequences (Lesage *et al*., 2015). Thus, there is an actual need to use lower doses of this organic product and, at the same time attain successful extraction or leaching of PTEs from the contaminated soil. Application of citric acid (CA) at a rate of 0.5mM only (approximately 10g L^{-1}) was capable to decontaminate Pb-polluted soil to some extent (Ash *et al.,* 2016). This rate seems to be safe, economical and comparable with root exudates i.e. 13.3-33.33 μmol g^{-1} plant dry weight (Gent *et al*., 2015). Thus, the current study is a trial to investigate the efficiency of using this organic acid (CA) at a low dose (10g L^{-1}) to decontaminate a shale deposit of Abu Thor in order to use this deposit safely as a soil conditioner for improving the physical and chemical characteristics of light textured soils. The kinetics of PTEs desorption from the shale deposit were a matter of concern in the current study.

2. Materials and methods

2.1. Site description

This site is located at Um Bogma Formation, Abu Thor locality (between longitudes 33° 22″ and 33° 23″ E and between latitudes 29° 00″ and 29° 02″ N), 40 km from the East of Abu Zeneima, Southwest Sinai (Egypt). A representative technological sample was collected from the shale deposit therein, crushed, ground to – 60 mesh size and a 0.5 g portion of the ground sample was acid digested by H_2SO_4, HCl, HNO_3 and HF then transferred volumetrically to a 100 mL conical flask. An alkaline solution was also prepared by fusion of 0.1 g of the ground sample with 1 g sodium hydroxide then dissolved in 1:1 HCl solution and diluted with distilled water up to 100 mL. These two solutions were used for determination of major and trace oxides i.e. Al_2O_3, Fe_2O_3, TiO_2, CaO, P_2O_5, MgO and SiO_2 according to Shapiro and Brannock (1962). Na and K contents were determined using flame photometric technique. Loss on ignition (L.O.I) was determined gravimetrically at 1000 °C for 2h. Total contents of PTEs namely Zn, Mn, Fe, Pb, Co and Ni, were also measured in the acid digest by a Unicam atomic absorption spectrometer model-969 (AAS) flame type and the results showed that this deposit contained (per kg) 630 mg Mn, 7704 mg Zn, 19200 mg Fe, 2627 mg Pb, 2763 mg Co and 1310 mg Ni.

2.2. Acid leaching protocol (ALP)

Shale deposit samples (≈0.580 kg) were uniformly packed over a piece of glass wool (supportive filtration media) at the bottom of PVC columns (6.8cm inner diameter× 45cm height, Fig 1). Citric acid (10 g L^{-1}) was then added to the shale deposit at the top of the column at a rate of 100 mL /100 min (≈1mL min^{-1}) with a total volume of 3200 mL of CA; on the other hand, the leachate was collected regularly every 100 min. This leachate was centrifuged, filtrated and analyzed for its contents of PTEs using atomic absorption spectrometer (Unicam 969, England). All chemicals were of analytical grade and the analyses were conducted in triplicates. Blank and spikes were also included to certify the obtained measures.

2.3 Data analyses

Figures were plotted via SigmaPlot 10. The removal efficiency (R.E.) of of each potentially toxic element was estimated according to Zheng et al. (2020) as follows:

$$\boldsymbol{R.E.} = \frac{\boldsymbol{\mu^0 - \mu}}{\boldsymbol{\mu^0}} \times \mathbf{100} \qquad \text{Eq 1}$$

where μ_0 is the initial content of metal ion in the shale deposit and μ is the corresponding content of this metal ion after PTEs extraction. The cumulative extracted amounts of PTEs (Zn, Mn, Fe, Pb, Co and Ni) with citric acid were then plotted vs time and fitted to six kinetic models as outlines by Sparks (1999) and Abbas and Salem (2011).

Zero kinetic model

$$Q_t = Q_0 - k_0 t \qquad \text{Eq 2}$$

First order model

$$\ln Q_t = \ln Q_0 - k_1 t \qquad \text{Eq. 3}$$

Second order model

$$\frac{1}{Q_t} = \frac{1}{Q_0} - k_2 t \qquad \text{Eq 4}$$

Power function

$$Q_t = at^b \qquad \text{Eq. 5}$$

Simple Elovich

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + (\frac{1}{\beta})\ln t \qquad \text{Eq. 6}$$

Parabolic diffusion

$$Q_t = Q_0 + K_p t^{1/2} \qquad \text{Eq 7}$$

where Q_t and Q_0 refer to extracted amounts of PTEs at time t (min) and at t=zero, respectively. The r^2 values and standard error of estimates (S.E.) were calculated to indicate the best model fitting the kinetics of PTEs extraction by citric acid.

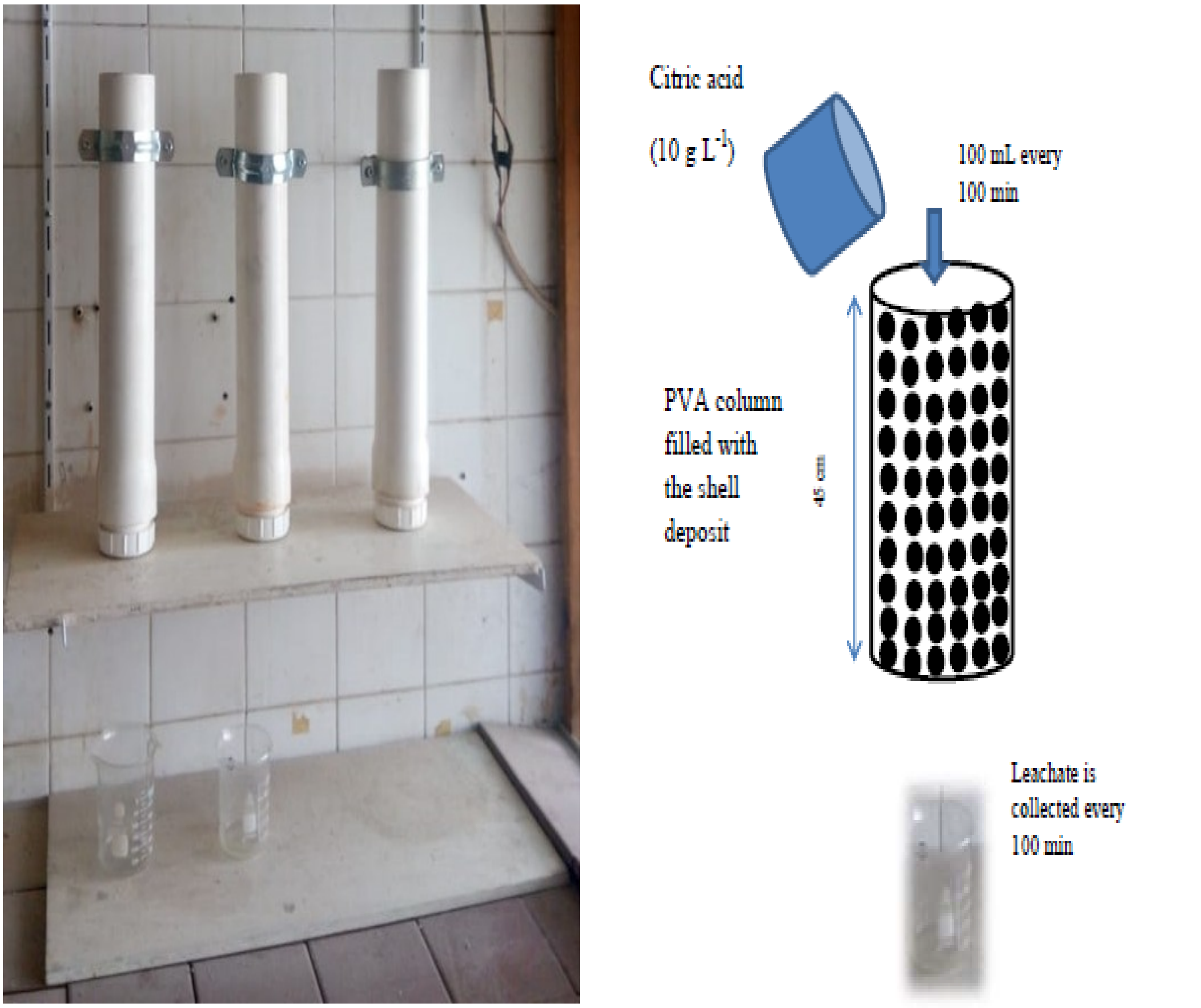

Fig. 1. Column experimental outline for the extraction of PTEs by citric acid (10 g L^{-1}).

3. Results and Discussion

3.1. *Characterization of shale deposit*

The dominance of silica in the shale deposit (37.35%) followed by alumina (18.37%) indicates the presence of one or more types of the clay minerals (Table 1). Ferric iron oxide and the lime contents were 18.38 and 4.61% ,respectively. It is worthy to mention that the loss of ignition (L.O.I) was 15.85% and this indicates the presence of water combined with the clay minerals in the shale deposit under investigation.

Table 1. Major and trace elements oxides (%) of the shale deposit.

Element oxide	%
SiO_2	37.35
AL_2O_3	18.37
TiO_2	0.12
Fe_2O_3	18.38
CaO	3.2
MgO	1.41
Na_2O	2.5
K_2O	1.62
P_2O_5	0.02
L.O.I	15.85
Total	98.82

3.2.Kinetics of PTE desorption from the shale deposit

Application of citric acid at a rate of 1 mL min^{-1} led, generally, to significant increases in the cumulative desorbed (extracted) amounts of PTEs as time passes. These amounts could be fitted via the different kinetic models as presented in Fig 2 and the calculated parameters of these fittings are presented in Table 2.

Based on the highest "r^2" values and the least S.E. ones, the power function seemed to be the best model fitting the kinetics of Zn, Mn, Fe, Pb and Co (Table 2). This might indicate that citric acid probably chelate more than one cation while soil washing; thus increased citric acid extraction efficiency of PTEs (Park *et al.*, 2013; Zhang et al., 2020) from the contaminated deposits. Moreover, the acidity of CA might increase the leaching efficiency of the investigated potentially toxic elements from the shale deposit.

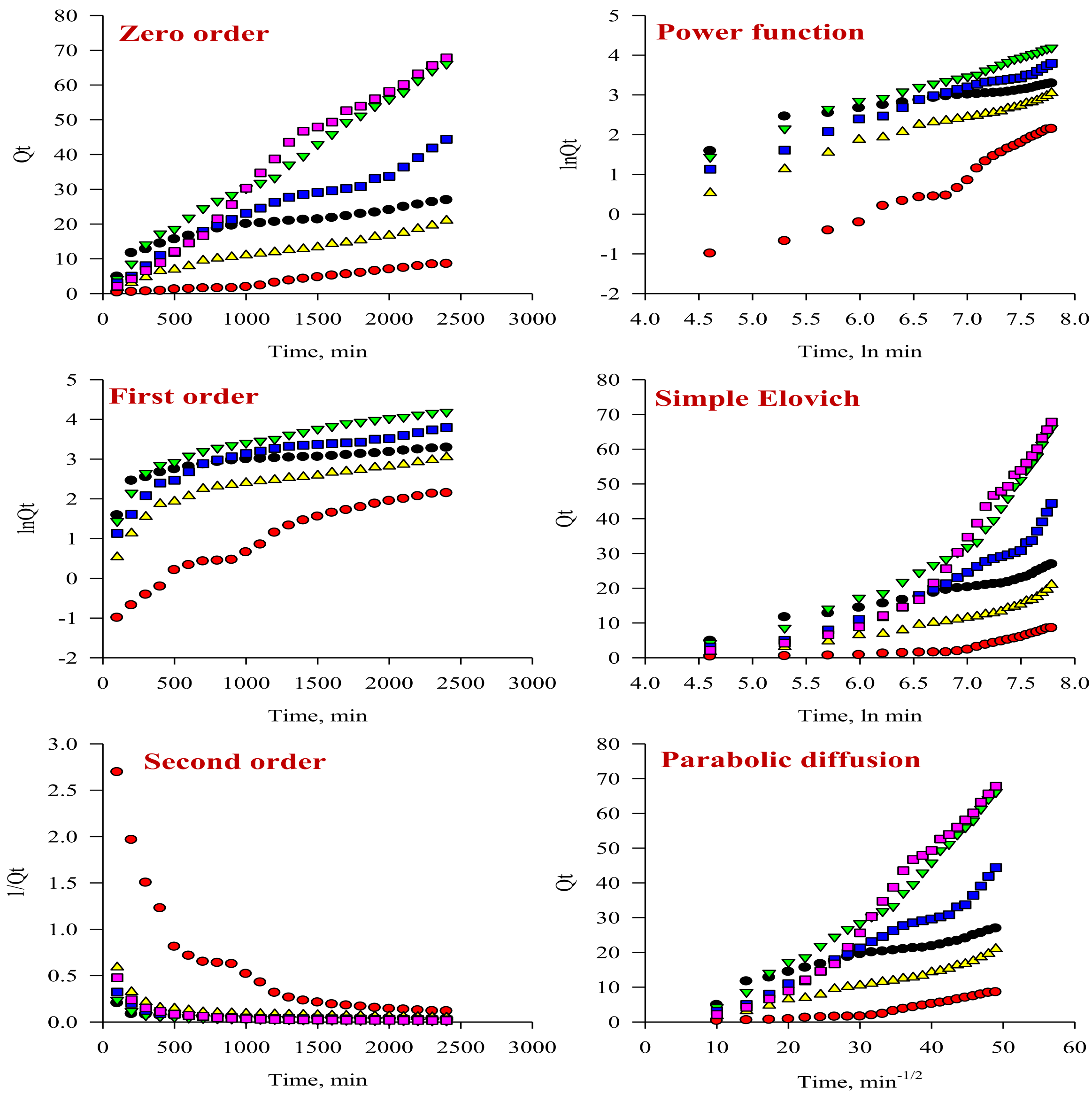

Fig. 2. Kinetics of PTEs desorption from the shale deposit of. Abu Thor .as affected by acid washing with citric acid (10 mg L-1).: Zn (●), Mn (○), Fe (▼), Pb (∆) , Co (■) and Ni (□).

The highest initial desorption rate (µg g^{-1} h^{-1}) was attained for Pb (0.1996), while the least ones was calculated for Mn (0.0005). The calculated values for Zn (0.0395), Co (0.0452), Ni (0.0515) and Fe (0.0968) although were relatively higher than that of Mn yet they were,generally, low. These findings illustrate that citric acid, at the used concentration and rate of flow,did not succeeded in extraction of thePTEs probably because these contaminants were found in the investigated shale deposits tightly bound to one or more of the shale components. Citric acid (CA) could probably release the easily bound forms of the investigated contaminants e.g. the soluble and exchangeable forms. These fractions are thought to possess the phyto-toxicity for plants when the shale deposit is used as a conditioner without further treatments.

Table 2. Rate parameters of PTEs desorption from shale sediments as affected by citric acid leaching (10 g L^{-1}) calculated the fitted kinetic models.

	Zn	Mn	Fe	Pb	Co	Ni
				Zero order model		
$Q_\circ$	1.9060	0.9858	5.9153	4.5405	3.2718	1.1284
$K_\circ$	0.0060	0.0039	0.0246	0.0056	0.0174	0.0280
r^2	0.9772	0.9837	0.9964	0.9274	0.9797	0.9868
S.E.	0.8114	0.4788	1.4114	1.4891	2.3868	3.0899
				First order model		
$lnQ_\circ$	1.0283	0.3616	2.5312	1.6222	2.1235	2.5312
k_1	0.0007	0.0010	0.0007	0.0005	0.0007	0.0007
r^2	0.6928	0.9095	0.8403	0.7389	0.8379	0.8403
S.E.	0.4740	0.3081	0.2841	0.3015	0.2932	0.2841
				Second order model		
$Q_\circ$	1.907	0.781	11.891	4.527	7.955	6.649
k_2	0.0002	0.0005	2.95×10^{-5}	7.1369×10^{-5}	4.434×10^{-5}	5.9223×10^{-5}
r^2	0.2658	0.5862	0.4192	0.4072	0.4527	0.3721
S.E.	0.3234	0.3953	0.0331	0.0821	0.0465	0.0734
				Power function		
a	0.0395	0.0005	0.0968	0.1996	0.0452	0.0515
b	0.7750	1.2476	0.8365	0.5784	0.8876	0.9235
r^2	0.9855	0.9861	0.9971	0.9678	0.9826	0.9895
S.E.	0.7031	0.4417	1.2714	0.9921	2.2099	2.7551
				Parabolic diffusion		
	-4.8945	-5.0372	-20.9000	-2.0639	-15.3825	-30.0061
	0.4355	0.2720	1.7479	0.4104	1.2292	2.0057
R2	0.9812	0.9287	0.9771	0.9715	0.9499	0.9830
S.E.	0.7996	1.0005	3.5541	0.9332	3.7471	3.5039
				Simple Elovich		
	-33.7523	-21.7141	-133.3819	-93.8815	-160.0817	-93.8815
	6.3798	3.7961	25.1383	17.5941	28.9861	17.5941
R2	0.9046	0.7773	0.8683	0.8361	0.8820	0.8361
S.E.	1.8025	1.7677	8.5188	6.7781	9.2225	6.7781

Sequence of removal efficiencies of PTEs from the shale sediment by citric acid

Fig 3A reveals that this organic acid extracted the investigated PTEs from the shale sediment following the sequence of Ni>Fe>Co>Pb≈Zn>Mn. The least amounts of extracted PTEs were recorded for each of Pb, Zn or Mn. Probably; these contaminantswere found in forms hardly to be removed by such a weak organic acid. Overall, the calculated removal efficiency values (Fig 3B) indicate the success of this organic acid in extraction of 11.2% Ni within only 3200 min of periodic leaching treatment with CA (10 g L^{-1}). Although, these results were below the expectations; yet this method seemed to be more applicable for long term enhanced phytoextraction (Lesage *et al*., 2015). Moreover, it exhibits low environmental toxicity (Angumeenal and Venkappayya, 2013).On the other hand, on-site treatmentsshould also be considered for the sediment leachate (loaded with toxic elements) to avoid its negative impacts on the surroundings. Although, Asaad *et al.* (2023) succeeded in improving considerably the quality of wastewater using portable units within only 72 h; yet their results were still below the expected (55–63.75%). Thus, further researches are needed in this concern.

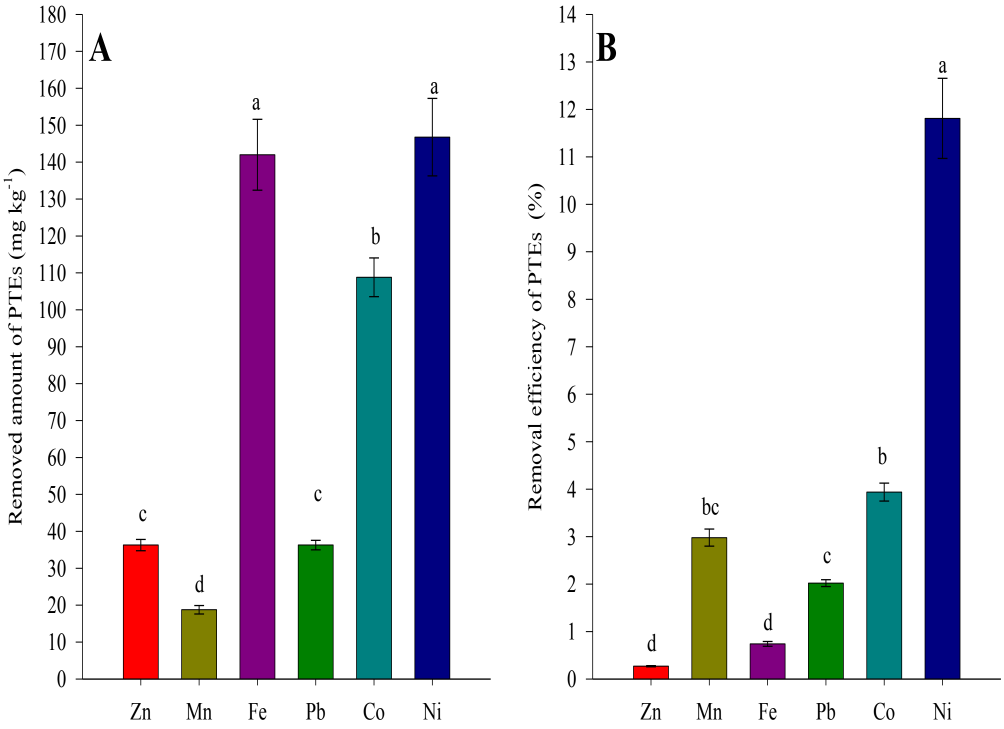

Fig. 3. Removal amounts (A) and efficiencies (B) of the investigated PTEs from the shale deposit after 3200 mL of citric acid extraction.

4. Conclusions

Extraction of PTEs with CA (10 g L^{-1}) can only remove the exchangeable or easily bounded PTEs in shale deposit; hence exhibited relatively low removal efficiency of PTEs from the shale deposit. However, it can be used for insitu long term facilitated phytoextraction to lessen the levels of PTEs in the shale deposit to reach more acceptable levels. Furthermore, citric acid should be tried at higher concentrations, different flow rates and even shale deposits of different chemical and mineralogical compositions to draw more obvious recommendations about its suitability for removing PTEs from shale deposits.

5. Conflicts of interest

There are no conflicts to declare.

6. Formatting of funding sources

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