



Contaminated soil amendment by diatomite: chemical fractions of zinc, lead, copper and cadmium

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Abstract

High concentration of labile metals in soil directly affects soil quality, water health and human safety. Decreasing mobility of metals, especially in contaminated soils, by cost-effective amendments may alleviate environmental problems. Natural diatomite was investigated to immobilize toxic elements of zinc, lead, copper and cadmium in a contaminated calcareous soil. The diatomite was characterized using X-ray fluorescence spectrometry and scanning electron microscopy. Contaminated soil was incubated with 0, 2 and 5 weight % of diatomite at 25 °C for 8 weeks. Tessier sequential extraction method was also used as a suitable method for identification of chemical forms of heavy metals; metal stability index and mobility factor were calculated. Results showed that application of diatomite in soil significantly decreased the metals in the exchangeable fraction and increased them in the residual fraction. The exchangeable metal fractions decreased by 66–88%, and residual fractions increased by 18–94% in the 5 weight % of diatomite treatment after 8-week incubation. With an increase in the amount of diatomite applied and the incubation time, metal mobility factor values significantly decreased and soil pH values increased. Application of diatomite caused the heavy metals redistribution toward more stable forms and leads to an increase in stability index values. In conclusion, in situ immobilization of heavy metals by application of diatomite, as a low-cost amendment, had a significant potential to stabilize metals in the contaminated calcareous soil.

Keywords Immobilization · Low-cost amendment · Mobility factor · Stability index · Sequential extraction

Introduction

Human activities are the main reasons for contamination of water, air and soil with heavy metals (Park et al. 2011). Contamination of soil is a kind of land degradation that arises when an amount of natural or anthropogenic components is more than maximum permissible amounts in soil (Liu et al. 2018). High concentration of metals, especially cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn), in soil can result in contamination of ground water due to movement of metals

via aqueous phase of soils and may affect food safety and environmental and human health (Hu et al. 2017).

Mobility of metals are controlled by soil factors, especially pH, clay content, calcium carbonate content and Fe and Mn oxides. Therefore, the chemical properties of soil and the soil processes (such as adsorption, desorption, precipitation and ion exchange) control relative proportions of heavy metal fractions from soluble and insoluble chemical forms (Jin et al. 2005; Powell et al. 2005).

Many remediation technologies, including physical, chemical and biological, have been used for solving the problem of heavy metal contamination in soils. Among those, in situ fixation of metals has been used as chemical remediation immobilizing heavy metal contamination in soil (Park et al. 2011; Sebastian and Prasad 2014; Souza et al. 2020).

Fractionation of heavy metals in soils by sequential extraction techniques has been applied in many studies for evaluation of chemical forms of metal (Huang et al. 2020; Alaboudi et al. 2019; Wang et al. 2018). Environmental risk of metals in contaminated soils is better predicted by

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sequential extractions determining relative proportions of various chemical forms containing metals as opposed to soil total digestion that gives information only about the total metal content (Powell et al. 2005). Available and unavailable forms of metals can be identified by sequential extractions of soils.

Many experiments have been investigated for determining ability of different compounds for stabilization of toxic metals in soils, such as nanomaterials, composts, manures, biochars, vermicomposts, calcium carbonate (CaCO_3), humic acids, zeolite and Na-zeolite (synthetic) (Ming and Boettinger 2001; Jordão et al. 2011; Houben et al. 2012; Bian et al. 2013; Rosen and Chen 2014; Egene et al. 2018; Palansooriya et al. 2019a, b; Shaheen et al. 2019; Souza et al. 2020). The usefulness of natural compounds in wide scale as cost-effective adsorbents is more influential than commercial synthetic adsorbents (Han et al. 2003).

Diatomite ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is a natural material that composed of accumulation of siliceous crusts diatoms (Al-Ghouti et al. 2009). It is applied for adsorption of metals from wastewater as a low-price adsorbent (Caliskan et al. 2011; Khraisheh et al. 2004; Miretzky et al. 2011). The ability of diatomite to adsorption of metal ions can be attributed to its unique physical and chemical properties such as highly porous structure, low thermal conductivity, well sorption, inertness, low density, high surface area (Al-Degs et al. 2001; Ye et al. 2015).

Although diatomite has been used as a natural material for sorption of toxic metals from aqueous solutions, there are confined studies on the application of Iranian diatomite in soils, especially heavy metal-contaminated soils. According to Ye et al. (2015), diatomite immobilized heavy metals in contaminated acidic soil. Chaiyaraksa and Tumtong (2019) reported the bioavailable index (BI) values of Zn, Cu, Cr and Ni decreased in contaminated acidic soils amendment by adding sepiolite, zeolite and diatomite. Huang et al. (2020) represented that modified diatomite can be applied for the immobilization of some metals in polluted soil. However, application of diatomite in contaminated soils as an amendment is not so common. The objective of this work was to ascertain chemical distribution of Zn, Cd, Cu and Pb in contaminated calcareous soil treated with different rates of diatomite as natural amendment (0, 2 and 5 weight %) in during of incubation (1, 2, 4 and 8 weeks). The remediation effectiveness was evaluated by determining the variations in metal mobility (MF) and their reduced partition index (I_R) in during incubation time. The experiments were performed over a period of 60 days in 2018 in soil science department, Urmia University, Iran.

Materials and methods

Diatomite characterization and soil physicochemical analyses

The soil was taken from the surface (0–20 cm) of contaminated area near a Pb and Zn mine in Zanjan Province ($48^\circ 25'$ east, $36^\circ 37'$ north), Iran (Hamzenejad and Sepehr 2017).

Diatomite sample was collected from Birjand mine as a natural adsorbent at North East of Iran ($59^\circ 36'$ east, $32^\circ 69'$ north). The nature diatomite was tested for morphology by scanning electron microscopy (SEM). The chemical analysis of raw diatomite was examined using X-ray fluorescence spectrometry (XRF). Surface area of adsorbent was measured by Sears' procedure (Sears 1956). The pH of diatomite was evaluated with a ratio of 1:5 diatomite/water.

Soil physical and chemical parameters were determined using standard methods: texture by the hydrometer technique (Gee and Bauder 1986), cation exchange capacity by sodium acetate 1 mol L^{-1} at pH 8.2 (Chapman 1965) and organic matter using Walkley–Black procedure (Walkley and Black 1934). Electrical conductivity and pH were measured with soil to water ratio in 1:5. Calcium carbonate (CaCO_3) equivalent was measured by titration (Horváth et al. 2005). Pseudo-total heavy metals contents of the soil were calculated by *aqua regia* digestion in a 1:3 v:v ratio of HNO_3 -HCl solution (Van Ranst et al. 1999). Availability of heavy metals was estimated by extraction with DTPA (Lindsay and Norvell 1978). All of these properties were determined in three replications.

Incubation experiments and sequential extraction procedures

Incubation experiment was carried out with three rates of diatomite (0, 2 and 5% w/w). Soil samples (0.5 kg) were mixed with 0, 10 or 25 g of diatomite in beakers with a plastic lid and incubated at 60% water-holding capacity, constant humidity and 25°C for 8 weeks. The chemical distribution of studied metals forms in the treated soil was evaluated using the Tessier method (Tessier et al. 1979). Soil samples were prepared at 1, 2, 4 and 8 weeks from each beaker for evaluating chemical forms of metals. The pH of subsamples (1:5 soil to water) was calculated in 1, 2, 4 and 8 weeks of incubation. Experiments were carried out in three replications for each treatment.

In brief, 1.0 g of incubated soil was putted in a 50-mL plastic centrifuge tube, and sequential extraction method was applied (Tessier et al. 1979):

F_1 : Exchangeable fraction (EXCH): The samples were reacted with 8 mL of 1 mol L⁻¹ MgCl₂, pH 7.0, at 25 °C for 1 h; F_2 : Carbonate fraction (CARB): The residue from (F_1) was reacted with 8 mL of 1 mol L⁻¹ NaOAc, adjusted to pH 5.0 with acetic acid (HOAc), at 25 °C for 5 h; F_3 : Fe & Mn oxides fraction (OX): The residue from F_2 was treated with 20 mL of 0.04 mol L⁻¹ NH₂OH.HCl in 25% (v/v) acetic acid at 95 °C for 5–6 h; F_4 : Organic matter fraction (OM): (a) The residue from F_3 was mixed with 3 mL of 0.02 mol L⁻¹ HNO₃ and 5 mL of 30% v/v H₂O₂ (pH=2) at 85 °C for 2–3 h; (b) +3 mL of 30% v/v H₂O₂ (pH=2) at 85 °C was added for 3 h; (c) +5 mL of 3.2 mol L⁻¹ NH₄OAC in 20% (v/v) HNO₃ was applied, the sample was diluted to 20 mL and was shaken continuously for 30 min; F_5 : Residual fraction (RES): The residue from F_4 was digested with 10 ml of HCl: HNO₃ (3:1) mixture at 95 °C for 2 h.

All steps were conducted by shaking horizontally at 200 rpm and centrifuged for 10 min at 2000 × g relative centrifugal force. The residual solids after extracting steps were washed with 8 mL water. The supernatant of each step was passed through the Whatman no. 40 paper and collected in plastic tube at 4 °C, and the content of Pb, Cd, Zn and Cu was measured by atomic absorption spectrophotometry (Shimadzu AA-6300).

The limit of detection (LOD) for metals explained as 3.3S blank/m (m: the slope of the calibration curve and S blank: the standard deviation for ten replicate measurements of blank) is 0.19, 0.37, 0.13 and 0.19 mg L⁻¹ for Cd, Pb, Cu and Zn, respectively. The limit of quantification (LOQ) (10S blank/m) is explained as the minimum value of analyte that can be superlatively and exactly evaluated. The LOQs of Cd, Pb, Cu and Zn are found to be 0.67, 1.01, 0.42 and 0.53 mg L⁻¹, respectively. The precision was determined as relative standard deviations (RSDs %) for ten replicate measurements of a solution containing 0.5 mg L⁻¹ of Cd, Pb, Cu and Zn and was found to be 3.27, 3.74, 1.71 and 2.27%, respectively.

MF and I_R

Mobility of metals was evaluated according to Yuan et al. (2011):

$$MF = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100 \quad (1)$$

where F_1 , F_2 , F_3 , F_4 and F_5 were concentration of metals at various steps by the Tessier sequential extraction method. The MF equation represented the ratio of Cd, Pb, Cu or Zn in the $F_1 + F_2$ fractions to the total content.

Metal stability and redistribution of metals in soil can be evaluated by the reduced partition index (I_R) (Han et al. 2003); I_R was calculated by the following formula:

$$I_R = \frac{\sum_{i=1}^{25} (F_i \times (i)^n)}{K^n} \quad (2)$$

i : The extraction step number (i : 1, 2, 3, 4 and 5 ($k=5$), F_i : The fractional percentage amount of metals and n : integer (generally 1 or 2). If all the metal is in F_1 fraction (exchangeable), the I_R has the minimum value ($I_R=0.04$); if it is all in F_5 fraction (residual), the I_R has the maximum value ($I_R=1$) (Han et al. 2003). The selection of n is optionally. When n is 2 represents the intensifying binding strengths of ions with developing in the steps of extraction and calculations easy.

Statistical analyses

The statistics were performed using SAS version 9.13 and SPSS 21.0. Two one-way analysis of variance (ANOVA) were applied to determine the effect of diatomite rate at each sampling time on measured variables and another one-way ANOVA to determine the effect of time at each diatomite rate. The comparison of means was carried out by the Tukey test at the 0.05 significance level, and the results were offered mean ± standard deviation (SD). Two-way ANOVA was conducted to explore the diatomite rate, incubation time and interaction of them on measured variables.

Results and discussion

Diatomite characteristics

The XRF results show that SiO₂ (73.2%), Al₂O₃ (11.60%), Fe₂O₃ (1.5%), MgO (1.5%), Na₂O (1%), K₂O (0.50%) and CaO (1.3%) are the chemical composition of diatomite.

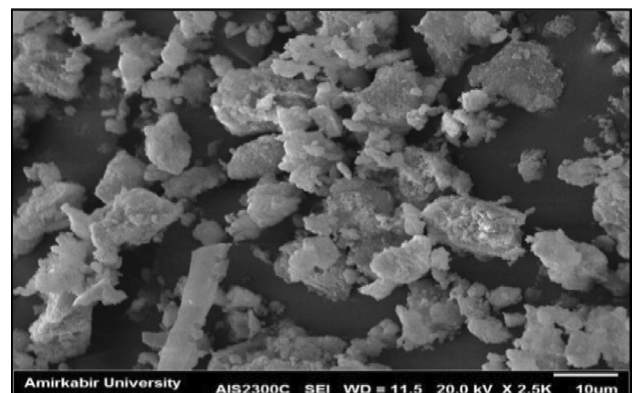


Fig. 1 Scanning electron micrograph (SEM) of diatomite

Microphotographs of diatomite are presented in Fig. 1. Diatomite frustules have two categories as centric and pennate shapes 10–200 μm (Khraisheh et al. 2004). Diatomite is composed of both centric and pennate types of shape for diatoms (Fig. 1). The surface area, pH and CEC of diatomite were estimated as 55 $\text{m}^2 \text{g}^{-1}$, 7.8 and 80 cmol kg^{-1} , respectively.

Contaminated soil

All the basic physico-chemical characteristics of soil sample are given in Table 1. Total amounts of Pb, Cd, Cu and Zn in soil were 7270, 471, 68 and 1612 mg kg^{-1} , respectively (Table 1). Based on Environmental Protection Agency (EPA), allowable values for Cd, Pb, Cu and Zn were 3, 300, 100 and 200 mg kg^{-1} , respectively (EPA 2012). Thus, total amount of metals was above the permissible limit. The DTPA-extractable concentrations of heavy metals (bioavailable) were significantly lower than the total concentrations, but were higher than allowable concentrations of the metals reported by Kaur and Rani (0.5, 10, 5 and 10 mg kg^{-1} for Cd, Pb, Cu and Zn, respectively) (Kaur and Rani 2006).

Effects of diatomite on the transformation of metal fractions

Cd and Pb fractions

The partitions of Cd in non-amended soil were F_2 : CARB (31%), F_3 : OX (28%), F_1 : EXCH (20%), F_5 : RES (16%) and F_4 : OM (5%) (Table 2). Application of diatomite decreased EXCH and CARB fractions of Cd in comparison with the control treatment (Table 2). Two-way ANOVA results showed that diatomite rate, incubation time and their interactions had a significant impact on chemical fractions of Cd in soil (Table 3). Diatomite rate ($F = 19085.3$) mostly influenced EXCH fraction of Cd in soil (Table 3).

The amount of EXCH fraction decreased from 20% (95 mg kg^{-1}) to 5% (28 mg kg^{-1}), and the CARB fraction decreased from 31% (144 mg kg^{-1}) to 29% (137 mg kg^{-1}) with addition of 5% diatomite and 8-weeks' incubation. The RES fraction of Cd increased with increasing diatomite

rate and incubation time (Table 2). Distribution of Cd in amended soil with application of 5% diatomite was as follows: RES (31%), OX (29%), CARB (29%), OM (6%) and EXCH (5%), demonstrating an increase in stable form of Cd in treated soil (Table 2). Diatomite dose, time and combined effect of them had the lowest impact on the OM and OX forms of Cd.

Diatomite has an alkaline pH ($\text{pH} = 7.8$), and incorporation of 2% and 5% diatomite raised pH of soil from 7.00 to 7.40 and 7.60, respectively, after 8-week incubation (Table 2), probably promoting formation of metal precipitates. Two-way ANOVA results demonstrated that pH of soil was mostly affected by diatomite rate ($F = 1060.9$) and the effects of time, diatomite rate and the interaction effect were mostly significant ($P < 0.001$) (Table 3). ElSayed (2018) reported that the removal efficiency of metals from wastewater by diatomite intensified as the value of pH, amount of adsorbent and contact time increased, whenever at $\text{pH} > 4$, the sorption of metals by diatomite reduced because of precipitation of metal ions.

However, in situ fixation mechanisms of metals by adsorbents in soil are probably different (Huang et al. 2017). They can immobilize metals via direct mechanisms such as physical–chemical attraction and precipitation, as well as indirect changes in soil properties, and thus decrease the availability of metals in contaminated soils (Sun et al. 2020). In calcareous soils, low metal available may be because of the sorption by CaCO_3 also the low desorption influenced by high pH as compared acidic soils (Hu et al. 2013). The amount of soluble phase of metals decreases with increasing pH, which lead to increase in unavailable forms of metals, and therefore reduced the mobility of metals in soil. In this study, the high amount of increase in pH of soil was looked after 8 week with application of 5% diatomite in soil (Table 2). The results of this study are confirmed with the other researches such as Radziemska et al. (2018), Ye et al. (2015) and Radziemska et al. (2017), who observed that the application of natural and modified diatomite intensified the value of pH in soil and consequently decreased labile forms of heavy metals.

Surface charges of diatomite are formed on ionizable groups, including $[\text{SiOH}_2^+]$ and $[\text{SiO}^-]$. Hydroxyl groups

Table 1 Soil properties

Sand %	Silt	Clay	Textural class	pH _(1:5)	EC dS m^{-1}	CEC $\text{cmol}_c \text{kg}^{-1}$	OM g kg^{-1}	CCE %
63	25	12	Sandy loam	7.05 \pm 0.14	0.15 \pm 0.03	9.59 \pm 0.23	5.8 \pm 0.12	13 \pm 0.34
Total metal concentration (mg kg^{-1})					DTPA extractable (mg kg^{-1})			
Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	
471 \pm 3.17	7270 \pm 4.76	68 \pm 2.33	1612 \pm 4.80	99 \pm 1.26	879 \pm 5.06	12 \pm 1.79	204 \pm 3.10	

EC: electrical conductivity, CEC: cation exchange capacity, OM: organic matter, CCE: calcium carbonate equivalent (mean \pm SD, $n = 3$)



Table 2 Changes in soil pH and chemical forms of metals in amended soil (%) with diatomite for 8 weeks of incubation

Diatomite(% w/w)	1 week			2 weeks			4 weeks			8 weeks		
	0	5%	2%	0	5%	2%	0	5%	2%	0	5%	2%
pH	7.01 ± 0.03c, A	7.18 ± 0.08b, C	7.18 ± 0.09c, A	7.01 ± 0.09c, A	7.21 ± 0.05b, B	7.02 ± 0.04c, A	7.31 ± 0.02b, A	7.46 ± 0.03a, B	7.03 ± 0.06c, A	7.4 ± 0.04b, A	7.61 ± 0.02a, A	
EXCH	20 ± 0.02a, A	19 ± 0.04b, A	17 ± 0.02c, A	20 ± 0.07 a, A	15 ± 0.01b, B	20 ± 0.07a, A	12 ± 0.29b, C	11 ± 0.08b, C	20 ± 0.19a, A	10 ± 0.03b, D	5 ± 0.01c, D	
CARB	31 ± 0.01a, A	30 ± 0.01b, A	30 ± 0.01b, A	31 ± 0.02a, A	30 ± 0.03b, A	30 ± 0.05b, A	30 ± 0.07 a, A	29 ± 0.04b, B	31 ± 0.06a, A	30 ± 0.11b, A	29 ± 0.03c, B	
Cd	28 ± 0.08a, A	28 ± 0.10a, A	28 ± 0.08a, B	28 ± 0.03 a, A	28 ± 0.06a, A	28 ± 0.02a, B	28 ± 0.02a, A	28 ± 0.11a, B	28 ± 0.31b, A	29 ± 0.10a, A	29 ± 0.23a, A	
OM	5 ± 0.02b, A	6 ± 0.20 a, A	6 ± 0.20 a, A	5 ± 0.03 b, A	6 ± 0.04a, A	6 ± 0.04a, A	6 ± 0.05b, A	6 ± 0.12a, A	6 ± 0.08a, A	6 ± 0.23a, A	6 ± 0.01a, A	
RES	16 ± 0.03b, A	18 ± 0.07a, D	19 ± 0.21a, D	16 ± 0.07 b, A	22 ± 0.07a, C	16 ± 0.26c, A	24 ± 0.04b, B	26 ± 0.03a, B	16 ± 0.04c, A	25 ± 0.11b, A	31 ± 0.33a, A	
EXCH	12 ± 0.02a, A	11 ± 0.01b, A	9 ± 0.03c, A	12 ± 0.02a, A	9 ± 0.01b, B	12 ± 0.01a, A	7 ± 0.01b, C	7 ± 0.03b, B	12 ± 0.01a, A	5 ± 0.02 b, D	4 ± 0.01c, C	
Pb	41 ± 0.03 a, A	41 ± 0.02a, A	41 ± 0.01a, A	41 ± 0.01a, A	41 ± 0.03a, A	41 ± 0.02a, A	41 ± 0.01a, A	41 ± 0.02a, A	41 ± 0.03a, A	41 ± 0.01a, A	41 ± 0.01a, A	
OX	17 ± 0.03a, A	17 ± 0.01a, B	17 ± 0.03a, A	17 ± 0.03a, A	17 ± 0.02 a, B	17 ± 0.01a, B	18 ± 0.02a, A	18 ± 0.01a, A	17 ± 0.02a, A	18 ± 0.01a, A	18 ± 0.03a, A	
OM	15 ± 0.05a, A	15 ± 0.04a, A	15 ± 0.04a, A	15 ± 0.01a, A	15 ± 0.02a, A	15 ± 0.04a, A	15 ± 0.05a, A	15 ± 0.02a, A	15 ± 0.07a, A	15 ± 0.02a, A	15 ± 0.03a, A	
RES	14 ± 0.01c, A	16 ± 0.02b, C	18 ± 0.03a, C	14 ± 0.03c, A	16 ± 0.05b, C	19 ± 0.07a, B	14 ± 0.06 b, A	19 ± 0.05a, B	14 ± 0.01c, A	20 ± 0.01b, A	22 ± 0.02a, A	
EXCH	17 ± 0.13a, A	13 ± 0.26b, A	10 ± 0.06c, A	17 ± 0.06a, A	10 ± 0.05b, B	6 ± 0.06c, B	17 ± 0.04a, A	8 ± 0.07b, C	4 ± 0.02c, C	4 ± 0.04b, D	2 ± 0.06c, D	
CARB	10 ± 0.06a, A	10 ± 0.06a, A	10 ± 0.02a, A	10 ± 0.04a, A	10 ± 0.03a, A	10 ± 0.05a, A	10 ± 0.04a, A	10 ± 0.06a, A	10 ± 0.04a, A	10 ± 0.01a, A	10 ± 0.03a, A	
OX	16 ± 0.15a, A	16 ± 0.04a, B	17 ± 0.06b, A	16 ± 0.07a, A	17 ± 0.18b, A	17 ± 0.16b, A	16 ± 0.08a, A	17 ± 0.20b, A	17 ± 0.04b, A	17 ± 0.13b, A	17 ± 0.06b, A	
OM	30 ± 0.078 a, A	30 ± 0.27a, A	30 ± 0.42a, A	30 ± 0.05a, A	30 ± 0.54a, A	30 ± 0.34a, A	30 ± 0.22a, A	30 ± 0.05a, A	30 ± 0.08a, A	30 ± 0.30 a, A	30 ± 0.03a, A	
RES	26 ± 0.30c, A	30 ± 0.02b, D	32 ± 0.03a, D	26 ± 0.28c, A	33 ± 0.39b, C	37 ± 0.15a, C	26 ± 0.34c, A	35 ± 0.11b, B	26 ± 0.35 c, A	39 ± 0.02b, A	40 ± 0.03a, A	
EXCH	12 ± 0.02a, A	10 ± 0.03b, A	8 ± 0.03c, A	12 ± 0.01a, A	9 ± 0.04b, B	7 ± 0.02c, B	12 ± 0.02a, A	7 ± 0.01b, C	12 ± 0.01a, A	5 ± 0.01b, D	4 ± 0.02 c, D	
CARB	18 ± 0.02a, A	18 ± 0.01a, A	18 ± 0.03 a, A	18 ± 0.04a, A	18 ± 0.03 a, A	18 ± 0.01a, A	18 ± 0.01a, A	18 ± 0.03a, A	18 ± 0.02a, A	18 ± 0.01a, A	18 ± 0.02a, A	
Zn	22 ± 0.04b, A	22 ± 0.01b, B	23 ± 0.02a, A	22 ± 0.02b, A	23 ± 0.01a, A	23 ± 0.02 a, A	22 ± 0.03b, A	23 ± 0.02a, A	23 ± 0.01a, A	23 ± 0.04b, A	23 ± 0.05a, A	
OM	11 ± 0.07a, A	11 ± 0.04a, A	11 ± 0.06a, A	11 ± 0.02a, A	11 ± 0.07a, A	11 ± 0.08a, A	11 ± 0.02a, A	11 ± 0.06a, A	11 ± 0.01 a, A	11 ± 0.06a, A	11 ± 0.03a, A	
RES	37 ± 0.03c, A	38 ± 0.05b, D	40 ± 0.04a, D	37 ± 0.04c, A	40 ± 0.15b, C	41 ± 0.09a, C	37 ± 0.01 c, A	42 ± 0.05b, B	43 ± 0.03a, B	44 ± 0.02a, A	44 ± 0.11a, A	

Means followed by the same letter within a row are not significantly different using one-way ANOVA at $P \leq 0.05$. The small and capital letters represent mean comparison at different rate of diatomite and different incubation time, respectively (mean ± SD, n = 3)

Table 3 Statistical significance of time and diatomite rate and their interactions on for variables of Cd in a two-way ANOVA analysis

Variables	Time	Diatomite rate	Time × diatomite rate
EXCH	6382.81***	19085.32***	1660.01***
CARB	13.61***	1166.43***	49.72***
OX	25.63***	16.42***	30.76***
OM	70.761***	44.08***	13.93***
RES	3661.52***	11876.08***	822.90***
pH	181.66***	1060.93***	35.10***
MF	8013.55***	30441.32***	2265.24***
Ir	58.73***	187.71***	20.29***

Significance effect: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

may obtain or miss proton in different values of pH as $\text{Si-OH} + \text{H}^+ \rightarrow \text{Si-OH}_2^+$ and $\text{Si-OH} + \text{OH}^- \rightarrow \text{Si-O}^- + \text{H}_2\text{O}$, respectively. The increase in RES fraction and decrease in EXCH fraction of Cd by application of diatomite could be due to the complex of Cd with surface groups of diatomite (Huang et al. 2020). Khraisheh et al. (2004) showed that the sorption processes of metals from aqueous solutions by diatomite were controlled by physical mechanisms.

The chemical distribution of Pb in non-amended soil was CARB (41%), OX (17%), OM (15%), RES (14%) and EXCH (12%) (Table 2). When soil was amended with diatomite (at 5% w/w) chemical forms of Pb were: CARB (41%), RES (22%), OX (18%), OM (15%) and EXCH (4%) after 8-week incubation. The EXCH, OX and RES fractions of Pb significantly affected by incubation time, diatomite rate and their interactions (two-way ANOVA results, see Table 4). Our present study further confirms that time, diatomite rate and their interactions mostly impact on EXCH and RES fractions of Pb in soil (Table 4).

Application of diatomite caused a significant decrease in EXCH fraction of Pb, and the percentage of reduction was 58% and 66% for treatment with 2% (w/w) and 5% (w/w) of diatomite, respectively, after 8-week incubation (Table 2).

Table 4 Statistical significance of time and diatomite rate and their interactions on for variables of Pb in a two-way ANOVA analysis

Variables	Time	Diatomite rate	Time × diatomite rate
EXCH	134603.86***	701833.41***	36053.75***
CARB	0.566 ns	1.95 ns	0.23 ns
OX	364.60***	664.08***	306.85***
OM	0.12 ns	0.99 ns	0.17 ns
RES	26726.24***	140851.27***	7665.55***
MF	37640.23***	194061.24***	10510.23***
Ir	340.50***	1648.50***	106.50***

Significance effect: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; ns: not significant

Also there is not a significant difference between with 2 and 5% (w/w) of diatomite in treated soil (Table 2). Application of diatomite increased the RES phase of Pb from 1023 mg kg^{-1} (14%) to 1648 (22%) mg kg^{-1} , an increase of 61% toward less available Pb (Table 2). The mechanisms for Pb immobilization in soils are sorption on oxides and clays and precipitation as carbonate, hydroxide or phosphate, complexation with organic matter, especially in soils with high pH (Zhang and Pu 2011). The application of diatomite significantly increased soil pH, so the stabilization mechanism of diatomite in studied soil could be ascribed mostly to the formation of $\text{Pb}(\text{OH})_2$ and Pb bounded to residual phase and Fe and Mn oxides that are low bioavailable (Abdelhafez et al. 2012).

Cu and Zn fractions

Before application of diatomite, Cu chemical fractions in soil were EXCH (17%), CARB (10%), OX (16%), OM (30%) and RES (26%) (Table 2). This result indicates that Cu to a large content is bounded to organic matter; the high amount of Cu was determined in the OM phase. The result from the two-way ANOVA for extracted forms of Cu in soil evaluated that the single effects of treatment on EXCH, OX and RES forms were mostly significant ($P < 0.001$), and that the interaction effect was highly significant as well ($P < 0.001$) (Table 5). In the amended treatment (2 and 5% diatomite), EXCH fraction of Cu decreased and the OX and RES forms increased, and there are no significant differences between 2 and 5% (Table 2). It appears Cu was adsorbed by diatomite, with active silanol and hydroxyl groups of diatomite accountable for sorption of metal ions (Caliskan et al. 2011). Hence, the presence of functional groups in diatomite and high amount of CEC of diatomite (80 cmol kg^{-1}) increased the surface complexation of heavy metals in soil. A similar result observed for in situ immobilization of Cu and Cd in soil with modified diatomite, labile forms of metals transformed the residual, reducible and oxidizable fractions

Table 5 Statistical significance of time and diatomite rate and their interactions on for variables of Cu in a two-way ANOVA analysis

Variables	Time	Diatomite rate	Time × diatomite rate
EXCH	5264.015***	44164.451***	1389.680***
CARB	0.624 ns	2.55 ns	0.1971 ns
OX	9.306***	257.807***	21.063***
OM	0.677 ns	0.12 ns	0.817 ns
RES	1266.868***	5974.570***	161.791***
MF	3866.984***	32199.050***	842.229***
Ir	649.333***	4249.333***	100.122***

Significance effect: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; ns: not significant

(Huang et al. 2020). Above pH 6 Cu precipitation as hydroxide, oxide or hydroxy carbonates is also possible, especially in calcareous soils (McBride 1994).

The EXCH forms of Zn decreased from 12% (non-amended) to 4% (treated with 5% diatomite), whereas the RES fraction increased from 37% (non-amended) to 44% (treated with 5% diatomite) (Table 2). With application of 2 and 5% (w/w) diatomite the value of EXCH form of Zn reduced from 5 to 4%, respectively, and the amount of RES fraction of Zn was 44%, after 8-week incubation (Table 2). So, there are not significantly different between application of 2 and 5% (w/w) of diatomite for immobilizing of Zn in polluted soil (Table 2). Two-way ANOVA results showed that time, diatomite rate and interaction of them had no significant effects on the CARB and OM fractions of Zn in soil (Table 6). According to F vales, diatomite rate, time and their interaction had most influences on the EXCH, RES and OX forms of Zn in soil, respectively (Table 6).

Table 6 Statistical significance of time and diatomite rate and their interactions for variables of Zn in a two-way ANOVA analysis

Variables	Time	Diatomite rate	Time × diatomite rate
EXCH	31491.18***	189804.04***	7955.71***
CARB	1.124 ^{ns}	9.32 ^{ns}	0.91 ^{ns}
OX	34.85***	457.52***	18.63***
OM	0.44 ^{ns}	4.73 ^{ns}	0.28 ^{ns}
RES	3286.11***	17584.25***	772.15***
MF	17185.21***	103814.14***	4383.37***
Ir	29.98***	185.77***	7.71***

Significance effect: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; ns: not significant

The fractions of Zn in non-amended soil: RES (37%), OX (22%), CARB (18%), EXCH (12%) and OM (11%). The forms of Zn were changed after treated with 5% diatomite and after 8-week incubation: RES (44%), OX (23%), CARB (18%), OM (11%) and EXCH (4%). The decreasing trend of EXCH fraction of Zn can be ascribed to the increase of soil pH in treated soil (Gusiatin and Kulikowska 2015). Zinc was redistributed from the EXCH form to the RES and OX fractions in treated soil (Shuman 1999). In general, when soil pH increases, metals tend to decline their labile fractions (Palansooriya et al. 2020). Moreover, the sorption mechanism of Zn on diatomite from water is controlled by physical process rather than chemical mechanism and sorption intensified by increasing of contact time (Caliskan et al. 2011).

I_R values of metals in soil

Fractionation of heavy metals could be explained by relative binding intensity (I_R) (Han et al. 2003). A high value of I_R indicates less availability of metals in soils (Han et al. 2003). In non-amended soil, I_R values were 0.35 for Cd, 0.37 for Pb, 0.53 for Cu and 0.54 for Zn (Table 7). Therefore, the I_R values showed that Cu and Zn were strongly bound to stable fractions (e.g., residual), whereas Cd and Pb were weakly bound, suggesting unstable fractions (e.g., exchangeable).

Two-way ANOVA results showed that diatomite rate, time of incubation and interaction of them had a significant effect on I_R values of metals in soil (Table 3 to Table 6). Diatomite rate had the most significant impact on I_R values of Cu (F -value = 4249), but diatomite rate had the lowest significant effect on I_R values of Zn (F -value = 185). The I_R values increased with application of diatomite and with incubation time (Table 7). Because by application of diatomite in soil metals are changed to stable forms, the

Table 7 The I_R values of metals in the incubated soil amended with diatomite

Incubation time (week)	Diatomite rate (% w/w)	Cd	Pb	Cu	Zn
1	0	0.35 ± 0.01 b, A	0.37 ± 0.02c, A	0.53 ± 0.02c, B	0.54 ± 0.04c, A
	2	0.37 ± 0.02 a, D	0.38 ± 0.01b, C	0.58 ± 0.04b, D	0.56 ± 0.02b, C
	5	0.39 ± 0.03a, D	0.40 ± 0.03a, C	0.60 ± 0.05a, D	0.58 ± 0.05a, B
2	0	0.35 ± 0.05b, A	0.37 ± 0.04b, A	0.54 ± 0.01c, AB	0.54 ± 0.03b, A
	2	0.41 ± 0.01a, C	0.39 ± 0.02a, C	0.61 ± 0.02b, C	0.57 ± 0.02a, C
	5	0.41 ± 0.03a, C	0.41 ± 0.01a, B	0.64 ± 0.04a, C	0.58 ± 0.05a, B
4	0	0.35 ± 0.04b, A	0.37 ± 0.04b, A	0.54 ± 0.01c, AB	0.53 ± 0.02b, A
	2	0.43 ± 0.01a, B	0.42 ± 0.05a, B	0.63 ± 0.04b, B	0.59 ± 0.03 a, B
	5	0.45 ± 0.03a, B	0.42 ± 0.02a, B	0.67 ± 0.03a, B	0.60 ± 0.01a, AB
8	0	0.35 ± 0.03c, A	0.37 ± 0.01b, A	0.55 ± 0.04b, A	0.54 ± 0.01b, A
	2	0.45 ± 0.01b, A	0.44 ± 0.01a, A	0.66 ± 0.02a, A	0.61 ± 0.03a, A
	5	0.50 ± 0.04a, A	0.45 ± 0.03a, A	0.68 ± 0.01a, A	0.62 ± 0.02a, A

Means followed by the same letter within a column are not significantly different using one-way ANOVA at $P \leq 0.05$. The small and capital letters represent mean comparison at different rates of diatomite and different incubation time, respectively, ± standard deviation (SD)

amended soil (with 5% w/w diatomite, after 8 weeks) had the I_R values 0.50 for Cd, 0.45 for Pb, 0.68 for Cu and 0.62 for Zn (Table 7). There is no significant difference between the low (2% w/w) and the high (5% w/w) rate of diatomite for I_R values, after 8-week incubation (Table 7). In the both non-amended and amended soil the highest I_R value was for Cu (0.53–0.68). Cu has more tendencies to complex with hydroxyl group as surface functional group of diatomite than Cd, Pb and Zn, so that the relative binding intensity of Cu was higher than them. This is similar to the conclusions reported by Huang et al. (2020).

In this study, when diatomite was applied to soil as amendment heavy metals were mostly fixed in the stable (residual) fraction. Therefore, addition of low-cost diatomite to polluted soil by heavy metals can decrease environmental risk because the I_R value is an indicator of heavy metal bioavailability in soil.

MF values of metals in soil

Mobility factor (MF) was used to assess mobility of metals in soil (Kabala and Singh 2001). Two-way ANOVA results showed that time, diatomite rate and their interaction had significant impacts on MF values of studied metals in soil (Table 3 to Table 6). MF of metals decreased after application of diatomite in during incubation (Fig. 2). Furthermore, in non-amended and amended soil, MF was higher for Cd and Pb than Cu and Zn (Fig. 2). This info shows a higher

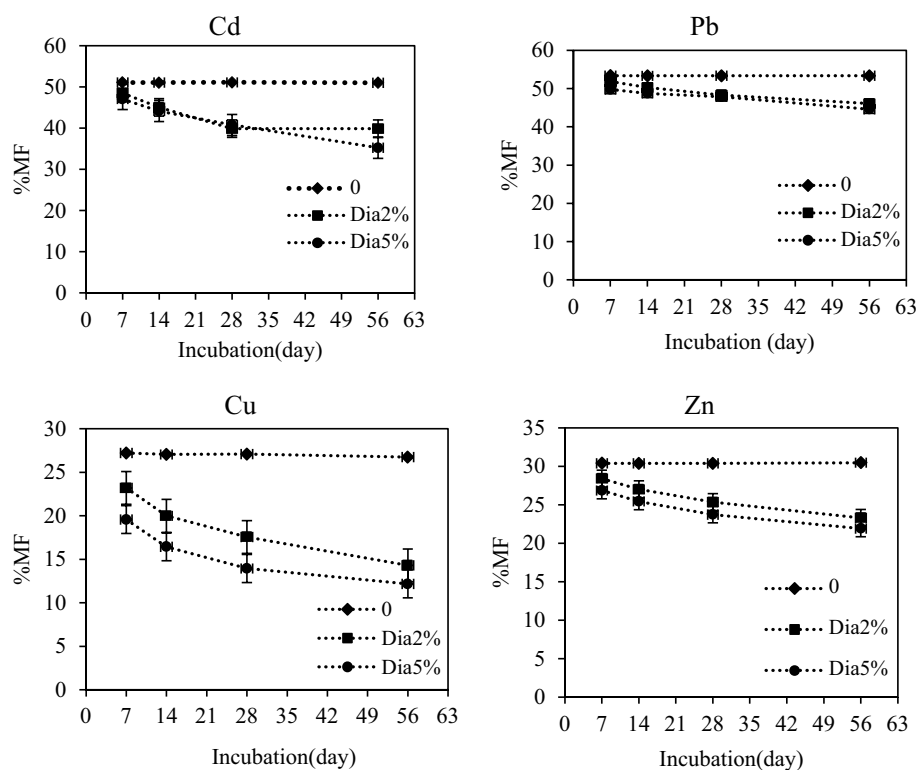
ratio of poor energy bonds (electrostatic) and as a result higher mobility of Cd and Pb in soil (Costa et al. 2014), and as also found Hamzenejad Taghliabad and Sepehr (2017).

After application of diatomite at 5% (w/w), MF of Cd, Pb, Cu and Zn reduced by 31, 16, 54 and 22 times, respectively. The reason for this result is that the content of EXCH fraction of metals decreased compared with the non-amended soil, whereas the soil content of OX and RES fractions increased in the amended soil. Therefore, bioavailability and mobility of metals were higher in non-amended than in amended soil, because of formation of stable complexes diatomite metal in soil. During incubation, the MF of metals in treated soil with the lower rate (2% w/w) of is very similar to 5% (w/w) of diatomite (Fig. 2). Application of diatomite decreased MF in the order of $Cu > Cd > Zn > Pb$. The lowest value of MF was received for Cu in amended soil (5% w/w diatomite).

Conclusion

Addition of diatomite significantly decreased the EXCH fraction and increased the RES fraction of studied heavy metals during incubation. Diatomite rate had the most significant impact on the distribution of chemical forms of metals in soil. The content of Cd, Pb, Cu and Zn in OM, OX and CARB fractions little changed when diatomite was applied. Forasmuch as, at the end of incubation, no

Fig. 2 The mobility factor (MF) of metals in the incubated soil amended with diatomite. Mean \pm standard error bars ($n=3$)



significant difference was found in use between high (5% w/w) and low (2% w/w) dose of diatomite, application of 2% of diatomite is recommend in a hypothetical remediation. Diatomite application decreased MF in order of $Cu > Cd > Zn > Pb$ because of increasing the stable metal fractions such as RES fraction. Moreover, the I_R value of metals increased after treatment by diatomite. Application of diatomite to soil led to a conversion of metals from labile to non-labile forms, hence potentially decreasing toxicity of metals in multi-metal-contaminated soil. The immobilization effects of natural diatomite on heavy metals in polluted calcareous soils need to be further assessed in the future, especially under field conditions.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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