

ORIGINAL ARTICLE

# Immobilization of Cadmium in a Cd-Spiked Soil by Different Kinds of Amendments

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## KEYWORDS

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**ABSTRACT:** Chemical stabilization of heavy metals is one of the soil remediation methods based on the application amendments to reduce mobility of heavy metals. A laboratory study was conducted to investigate the influence of different kinds of amendments on cadmium (Cd) stabilization in a Cd-spiked soil. The amendments were municipal solid waste compost (MSWC), Coal fly ash (CFA), rice husk biochars prepared at 300°C (B300) and 600°C (B600), zero valent iron (Fe<sup>0</sup>) and zero valent manganese (Mn<sup>0</sup>). The Cd-spiked soils were separately incubated with selected amendments at the rates of 2 and 5% (W/W) for 90 days at 25 °C. Soil samples were extracted by EDTA for periods of 5 to 975min. In addition, sequential extraction was used as a suitable method for identification of chemical forms of Cd and their plant availability. The addition of amendments to soil had significant effects on desorption and chemical forms of Cd. Changes in Cd fractions and their conversion into less soluble forms were clear in all treated soils. The addition of amendments resulted in a significant reduction in mobility factor of Cd compared to the control treatment. Among all amendments tested, Fe<sup>0</sup> was the most effective treatment in decreasing dynamic of Cd. Biphasic pattern of Cd desorption kinetic was fitted well by the model of two first-order reactions. In general, from the practical point of view, Fe<sup>0</sup>, MSWC and Mn<sup>0</sup> treatments are effective in Cd immobilization, while application of Fe<sup>0</sup> at 5% (W/W) was the best treatment for stabilization of Cd.

## INTRODUCTION

Environmental pollution by heavy metals is one of the major problems faced by many developing countries, such as Iran. Cadmium (Cd) is one of the heavy metals present in contaminated soils, which may cause long-term dangers to environments and humans [1]. Several

anthropogenic sources including chemical fertilizers, sewage sludge, pesticides, and burning of fossil fuels are the major sources of Cd in contaminated soils[1].The mechanisms of adsorption desorption and precipitation–dissolution are important process in controlling the fate of heavy metals [2].Stabilization of heavy metals is a

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common practical method, which decreases the hazard potential of heavy metals through transforming the mobile forms of contaminants into less mobile [3]. Low-cost and widely available amendments with low environmental impact are used for the immobilization of heavy metals. Several natural or synthetic materials including phosphate-based amendments [4], bio solids [5], iron and/or manganese (hydrated oxides and  $\text{Fe}^0$ ) [6], and lime [7] were tested to evaluate their ability to immobilize Cd. Desorption of Cd in calcareous soils was studied by others [8, 9], but the effect of immobilizing amendments on Cd desorption in calcareous soil has not been reported. Hence, it is necessary to understand the effect of soil amendments for reducing the mobility of Cd in calcareous soils.

Therefore, the aim of this study was to evaluate the effects of coal fly ash, municipal solid waste compost, two types of biochar of rice husk prepared at 300 and 600°C, zero valent iron and zero valent manganese on the release and chemical transformation of Cd in a Cd-spiked soil, and to compare the ability of these amendments to reduce the mobility of Cd in a

contaminated soil via desorption kinetic and sequential extraction experiments.

## MATERIALS AND METHODS

In order to investigate the influence of different kinds of amendments on the release and chemical forms of Cd, a soil sample was collected (Fine, mixed, mesic, Fluventic Calcixerepts) from Shiraz, Fars Province, Iran. Particle size distribution was determined by the hydrometer method [10]. The pH values of the soil were measured in a 1:1 soil-water and electrical conductivity (EC) was measured in the soil paste extracts. Cation exchange capacity (CEC) and organic matter (OM) were determined by replacing cations with NaOAc [11] and Walkley-Black method [12], respectively. The calcium carbonate equivalent (CCE) was determined by neutralization with HCl [13]. DTPA-extractable heavy metals were determined by flame atomic absorption [14]. Total heavy metals were extracted by  $4\text{HNO}_3$  [15]. The selected properties of soil are presented in Table 1.

**Table 1.** Selected chemical and physical properties of studied soil.

Property	Value	Property	Value
pH	7.8	Soluble Fe in DTPA ( $\text{mg kg}^{-1}$ )	4.1
CCE (%)	39.5	Soluble Cu in DTPA ( $\text{mg kg}^{-1}$ )	0.92
Sand (%)	27	Soluble Mn in DTPA ( $\text{mg kg}^{-1}$ )	5.6
Clay (%)	35	Soluble Pb in DTPA ( $\text{mg kg}^{-1}$ )	Trace
OM (%)	1.4	Soluble Cd in DTPA ( $\text{mg kg}^{-1}$ )	Trace
CEC ( $\text{Cmol}(+) \text{kg}^{-1}$ )	15.8	Total Cd ( $\text{mg kg}^{-1}$ )	Trace
EC ( $\text{dS m}^{-1}$ )	0.65	Total Fe ( $\text{mg kg}^{-1}$ )	30554

Various amendments were used for their abilities to decrease Cd mobility in Cd-spiked soil: coal fly ash (CFA), municipal solid waste compost (MSWC), rice husk biochars prepared at 300°C (B300) and 600°C (B600), zero valent iron ( $\text{Fe}^0$ ) and zero valent manganese ( $\text{Mn}^0$ ). CFA and MSWC were collected from Zarand coal washing factory and recycling and

municipal solid waste compost factory of Kerman, Iran, respectively. Biochars were prepared at 300°C and 600°C from rice husk. Husk samples (covered with aluminum foil) were placed in a furnace for 4h to produce biochars. Zero valent iron ( $\text{Fe}^0$ , 99.5%, in the form of iron grit) and zero valent manganese ( $\text{Mn}^0$ , 99.5%, in the form of manganese grit) were used in

present study. The selected properties of amendments used are presented in Table 2. In addition, Fourier Transform Infrared Spectroscopy (PerkinElmer FT-IR: Spectrum RXI) was used for the recognition of the morphology and structure of the produced biochars (Figure 1).

For incubation experiment, soil samples were placed in plastic and Cd was added at the rate  $500\mu\text{g g}^{-1}$  as Cd  $(\text{NO}_3)_2$ . Selected amendments were added to each soil sample separately, at two levels (2 and 5% W/W) (Table 3), and each soil sample was mixed thoroughly. The soil samples were incubated for 90 days at  $25^\circ\text{C}$ . The moisture was kept at field capacity (FC). After incubation, samples were air-dried and used for Cd desorption and fractionation study.

Soil Cd was fractionated to seven fractions [16]. Table 4 provides an outline of the Singh et al. [16] procedure. Residual forms (Res) is calculated by subtracting sum of six fractions from total Cd. Cd mobility was evaluated by a mobility factor [17] which calculated according to the equation:  $(\text{Ex} + \text{Car} / \text{sum of fractions}) \times 100$ .

Desorption kinetics of Cd was studied by means of batch-type experiments. Five g of each soil samples, in triplicate, was placed in polyethylene tubes and extracted separately with 25 ml of 0.01 M EDTA. Soil samples were shaken for periods of 0.08 to 16.25 h (0.08, 0.25, 0.58, 1.25, 2.25, 4.25, 8.25, 16.25 h) at  $25 \pm 2^\circ\text{C}$  and then centrifuged immediately at 2500 rpm. The supernatant were filtered through filter paper and Cd concentration was determined using AAS (Shimadzu AA-670G).

Table 2. Selected chemical composition of amendments.

Amendments		Chemical Properties				
CFA	*SiO <sub>2</sub> (%)	*Al <sub>2</sub> O <sub>3</sub> (%)	*TiO <sub>2</sub> (%)	*Fe <sub>2</sub> O <sub>3</sub> (%)	*CaO (%)	
	46.47	27.32	0.9	6.73	4.56	
	*BaO (%)	*SrO (%)	*MgO (%)	*K <sub>2</sub> O (%)	*Na <sub>2</sub> O (%)	
	0.15	0.14	2.32	3.42	0.82	
	*SO <sub>3</sub> (%)	*P <sub>2</sub> O <sub>5</sub> (%)	*Mn <sub>3</sub> O <sub>4</sub> (%)	pH	**C (%)	
	4.6	4.6	0.82	9.1	67	
**H (%)	**N (%)	**O (%)	-	-		
3.8	3.92	0.96	-	-		
MSWC	pH	EC (dS m <sup>-1</sup> )	OM (%)	Cu (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	
	7.4	19.36	38	19	28	
	Fe (mg kg <sup>-1</sup> )	Mn (mg kg <sup>-1</sup> )	Pb (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Ni (mg kg <sup>-1</sup> )	
25	11	13.3	0.28	1.2		
B300	pH	EC (dS m <sup>-1</sup> )	**C (%)	**H (%)	**N (%)	
	6.2	13.1	41.57	2.11	1.52	
B600	8.7	21.2	48.99	1.55	Trace	

\* Determined by X-ray fluorescence (XRF) analyzer; \*\* Determined by CHN analyzer

**Table 3.** Experimental design for incubation experiment.

Treatment	Amendment (applied rate %)	Treatment	Amendment (applied rate %)
S1	MSWC (2%)	S7	B600 (2%)
S2	MSWC (5%)	S8	B600(5%)
S3	CFA (2%)	S9	Fe <sup>0</sup> (2%)
S4	CFA (5%)	S10	Fe <sup>0</sup> (5%)
S5	B300 (2%)	S11	Mn <sup>0</sup> (2%)
S6	B300 (5%)	S12	Mn <sup>0</sup> (5%)

**Table 4.** Summary of the Sequential extraction procedure used in this study.

g soil:mL solution	Extracting solution	Shaking time (h)	Chemical form of Cr	Symbol
10:40	1 M Mg(NO <sub>3</sub> ) <sub>2</sub>	2	Exchangeable	EX
10:40	1MNaOAc (pH=5 CH <sub>3</sub> COOH)	5	Carbonate- bound	Car
10:20	0.7MNaOCl (pH=8.5)	0.5 in boiling water	Organically- bound*	Om
5:50	0.1MNH <sub>2</sub> OH.HCl (pH=2 HNO <sub>3</sub> )	0.5 in boiling water	Mn-oxide- bound	Mn-OX
5:50	0.25MNH <sub>2</sub> OH.HCl+ 0.25MHCl	0.5 at 50 °C in water	AmorphousFe-oxide-bound	FeA-Ox
5:50	0.2M (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +0.2M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> +0.1 MC6H8O6	0.5 in boiling water	CrystallineFe- oxide-bound	FeC-Ox

\*Two times extraction

Two first-order kinetic models were used as an approximate method for describing Cd desorption. A two first-order reaction model can divide Cd into three fractions [18, 19], Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>3</sub>, where:

$$q = Q_1(1 - e^{-k_1t}) + Q_2(1 - e^{-k_2t})$$

$$Q_3 = q_{\text{total}} - Q_2 - Q_1$$

q represents amount of Cd released at time t.

Q<sub>1</sub> (mg kg<sup>-1</sup>): “labile” fraction, readily extractable, associated to the rate constant k<sub>1</sub>.

Q<sub>2</sub> (mg kg<sup>-1</sup>): “moderately labile” fraction, less extractable, associated to the rate constant k<sub>2</sub>.

Q<sub>3</sub> (mg kg<sup>-1</sup>): Cd fraction, which is not extractable

q<sub>total</sub>: total concentration of Cd in soil.

This model was tested by coefficients of determination (R<sup>2</sup>) and standard errors of estimate (SE).

The standard error was calculated as follows:

$$SE = \left[ \frac{\sum(E - E')^2}{n - 2} \right]^{0.5}$$

Where E and E' are the measured and calculated amounts of Cd release in soil at time t, respectively, and n is the number of measurements. The regression of nonlinear procedure and other statistical analyses were calculated by Microsoft Excel 2007.

## RESULTS AND DISCUSSION

### Characterization of Biochars amendments

According to the results of biochars analysis, elimination of unstable compounds at the higher temperatures caused biochars to have higher percentages of carbon (C) while much lower hydrogen (H) and nitrogen (N) contents (Table 2).

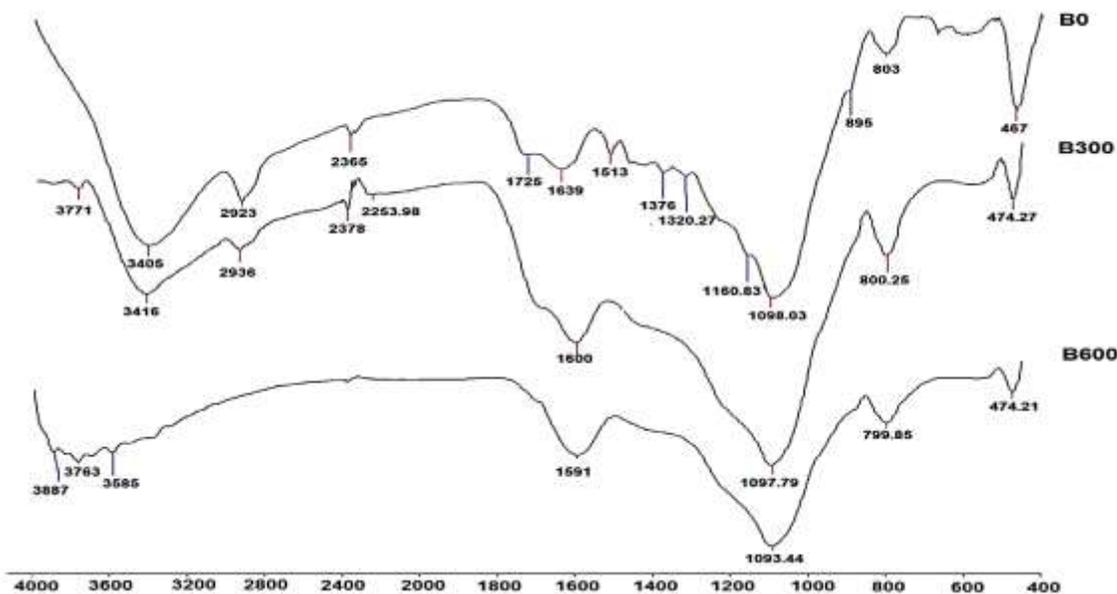


Figure 1. FTIR spectra of rice husk before pyrolysis (B0), B300, and B600.

Increased pyrolysis temperature led to increased pH (from 6.2 to 8.7) and EC (from 13.1 to 21.2 dS m<sup>-1</sup>). Figure 1 shows the FTIR spectra of rice husk before pyrolysis (B0), B300, and B600. The sharp peak at 3405 and 3416 cm<sup>-1</sup> in B0 and B300, and the weak peaks at around 3585 cm<sup>-1</sup> in B300 and B600 are due to hydroxyl group (–OH) stretching and functional group of phenol. The peaks at 2923 cm<sup>-1</sup> and 2936 cm<sup>-1</sup> seen in B0 and B300, are ascribed to aliphatic C–H deforming vibration and functional group of alkanes. These functional groups disappear at temperatures higher than 600°C. The weak band at 1725 cm<sup>-1</sup> for B0, which disappear at temperatures higher than B300, is assigned to C=O stretching in carbonyl group and neutral functional group of aldehydes. The weak band at around 1640 cm<sup>-1</sup> for B0 is due to the presence of or C=C stretching (functional group of alkenes). The weak band 1539 cm<sup>-1</sup> for B0 indicates the presence of N–O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300 °C indicating the volatilization of nitrogen forms. The band at around 1600 for B300 and B600 indicated the presence of aromatic C=O ring

stretching (likely –COOH) or C=C stretching of aromatic. This band is stronger in B600 compared to B300, which for this reason; pH was higher than biochar produced in low temperature. The weak bands at 1320 cm<sup>-1</sup> and 1376 cm<sup>-1</sup> in B0 indicate the presence of the N–O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300°C indicating the volatilization of nitrogen forms. The band at around 1090 cm<sup>-1</sup> is due to aliphatic ether, alcohol C–O or aromatic stretching in cellulose and hemicelluloses. In general, the results from FTIR analysis of B600 showed the functional groups such as carboxylic bonds and aromatic C=O ring stretching (likely –COOH) was higher than B300, which increased its pH.

#### Effects of amendment on Cd fractionation

Figure 2 shows the chemical forms of Cd in treated soils and control soil. Sequential extraction experiment showed that Cd was mostly in the Car form in all soil samples, since the soil in present study is highly calcareous (CCE: 39%). Rajaei et al. [20] reported that

in calcareous and alkaline soils of Iran, Car fraction was higher than the other fractions of Cd in amended soils with cadmium-enriched compost. Cd was predominantly connected with Car fraction (about 40-44%) in calcareous soils [21]. For control treatment, Car and Res form was 51.6% and 35.77%, respectively. According to the results, the first two steps of fractionation producers extracted more than half of Cd applied to control soil.

Among the chemical fractions of heavy metals, EX and Car fractions usually determine the real environmental risk. Hence, evaluation on the changes in the EX and Car forms could be used to assess the effect of the selected amendments on Cd immobilization. With application some amendment, EX Cd significantly decreased. As results, chemical form of EX was significantly decreased when soils were amended by  $\text{Fe}^0$ , MSWC,  $\text{Mn}^0$  at application rates of 2% and 5%. The lowest EX form is associated with application of  $\text{Fe}^0$  especially at high rate (5%). Addition of  $\text{Fe}^0$  into soil led to formation of amorphous iron oxides by oxidizing

process [22]. Metal oxides such as Fe and Mn oxides adsorbed Cd on the surface OH groups via Cd-proton exchange or at the negatively charged surface sites [23]. Reduction of EX form in  $\text{Fe}^0$ -treatment soil is due to the formation of iron oxide, and so increased the sorption or co-precipitate of Cd in soils. Watanabe et al. [24] studied the effect of  $\text{Fe}^0$  on availability of Cd in Cadmium-Contaminated Soils. Their results showed that application of  $\text{Fe}^0$  increased the free-oxides-occluded (less available) Cd content, and decreased the exchangeable and iron-manganese-oxides-bound (more available) Cd content, in Cd-contaminated soils. Application of industrial iron and steel slag amendment decreased EX form of Cd by 100% and increased oxide fraction of Cd by 50% [25]. Application of B300 increased Ex fraction of Cd. It seems that lowering pH in B300-amended soil probably increased the mobile fraction (EX) of Cd in soils. There was not a statistically significant different between other treatment as compared the controls soil in EX form.

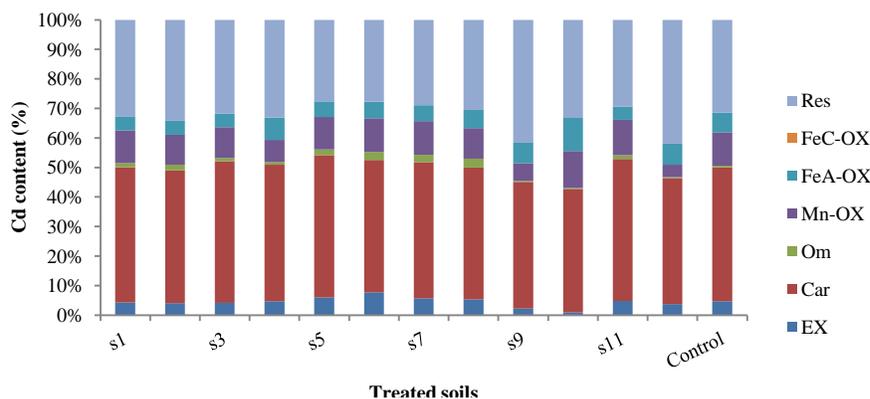


Figure 2. Percentages of the various fractions of Cd in amended soil.

Amendments addition also had effects on the other Cd fraction in soil samples. All amendments significantly decreased Car fraction. The reduction in EX form of Cd in amended soils followed the sequence of  $\text{Fe}^0 > \text{B600} = \text{Mn}^0 > \text{MSWC} > \text{CFA} > \text{B300}$ . Application of organic sources (B300, B600 and MSWC) considerably increased mean of Om fraction compared to control soil.

Organic amendments could contribute to the reduction of metal dynamic by declining the labile metal pools in soil [26]. In addition, this amendment could redistribute heavy metals from labile forms to less mobile forms [27, 28] and reduce their availability to plants. The FeC-OX fraction in all soil samples was lower than the detection limit of AAS. This shows the low affinity of Cd to enter

crystalline iron oxide form under the conditions of present study. This was in agreement with the results of Rajaei et al. [20]. Addition of amendments decreased FeA-OX and Mn-OX fractions as compared to control. On the other hand, the Res fraction did not show a clear trend in treated soil. Knox and Adriano [29] studied the effect of various amendments, including lime, apatite, natural zeolite, Fe oxides, and N-viro (an alkaline stabilized sewage sludge), on reduction of Cd mobility. Their results showed that Fe oxides, apatite, and N-viro were more effective in reducing Cd availability than lime or zeolite. Houben and Sonnet [30] tested the application of zero valent iron on phytoavailability of Zn and Cd in a contaminated soil. They showed that phytoavailability of Zn and Cd was reduced by 63% and 45% respectively when soil was treated with 5% (w/w) iron grit. Heavy metals dynamic depends on their chemical forms. The results show that soil amendments reduced Cd mobility. In control soil, the mobility factor was 56.98%. The mobility factor in S1-S12 samples was 50.02, 49.04, 52.13, 50.95, 54.18, 52.54, 51.84, 49.92, 45.06, 42.57, 48.70, 47.68, and 56.98 respectively. The lowest mobility factor is associated with application of Fe<sup>0</sup> especially at high rate (5%). These results confirm the effectiveness of Fe<sup>0</sup> in stabilizing of Cd in contaminated soils, as previously reported [30, 29]. In general, the reduction of dynamic of Cd in the soils amended with different amendments followed the sequence of Fe<sup>0</sup> > Mn<sup>0</sup> > MSWC > B600 > CFA > B300. Therefore, Fe<sup>0</sup> was considered best for immobilization of Cd in soil in fractionation experiment.

#### *Effects of amendment on Cd release*

Desorption patterns of Cd were similar in all samples; although amount of Cd released in the treated soils (Except for B300<sub>5%</sub>) was higher than the control (Figure 3). Biphasic pattern was observed in all samples: primary rapid desorption at the beginning time (0.58 h) and followed by a slow reaction, until the curve appeared flat and equilibrium was obtained (2.25 h). Cd

extracted in the begging time may be related to most labile fractions, while with time, the labile pool from more recalcitrant fractions was extracted [31]. Two-step release process of heavy metals was observed by others [18, 32].

Results from desorption of Cd showed that the effects of amendments were significant on desorbed Cd. Soils treated with amendments had a higher capacity for stabilization of Cd compared to control soil. The Cd released by 0.01M EDTA varied from 109.18 to 262.5 mg kg<sup>-1</sup>. The highest amount of desorbed Cd was from B300<sub>5%</sub>-treatment with 262.5 mg Cd kg<sup>-1</sup> soil. The lowest amount of desorbed Cd was from Fe<sup>0</sup><sub>5%</sub>-treatment with 109.18 mg Cd kg<sup>-1</sup> soil. Addition of Fe<sup>0</sup> at the rates of 2 and 5% considerably decreased Cd release by 43.99% and 49.91%, respectively, compared to control soil. Friesl et al. [33] showed that iron- rich bauxite residue treatment reduced the lability of Cd up to 91 on a contaminated sandy soil. Application of Mn<sup>0</sup> decreased Cd release by 14.4 and 19.5% at the rates of 2 and 5%, respectively. Chen et al. [5] studied effect of various amendments on mobility of Cd and showed that addition of manganese oxide reduced the extractability of Cd in soils, and significantly reduced the uptake of Cd by wheat shoots. The MSWC application at the rate of 2 and 5% led to reduction Cd desorption by 29.6 and 35.17%, respectively. Composted bio solid amendments could be useful in decreasing Cd uptake by plants from contaminated soil [25]. It was expected that addition of CFA in soil decreased Cd release efficiently. However, addition of CFA at the rates of 2 and 5% decreased Cd release by 1 and 1.37%. Reduction of heavy metal mobility by CFA is due to two mechanisms: Increasing pH and specific surface area, which causes the precipitation of insoluble phases and promoting metal sorption via surface complexation. Treatment with B600 at the rates of 2 and 5% decreased the Cd release by 14.4 and 10.4. Release of Cd increased when soils were amended by B300 at application rates of 2% and 5%. The application of 2 and 5% B300 led to increasing Cd

desorption by 17.43 and 20.4%. The results obviously exposed that application of B300 decreased soil pH, so increased the Cd dynamic. According to the results, amendments application at 5% (W/W) is more effective (Except for B300) than low addition level (2% W/W) for reducing Cd availability. Availability of Cd can be decreased in soils via different mechanisms including ion exchange, co-precipitation, electrostatic attraction, physical adsorption, and surface complexation.

It seems that, surface complexation plays an important role in the Cd immobilization in Fe<sup>0</sup> and Mn<sup>0</sup>-treated soils. In other words, Fe<sup>0</sup> and Mn<sup>0</sup> decreased availability of Cd in soils, due to adsorption of Cd on surface of

these amendments, which provides large surface area. Stabilization of Cd in soils with application of MSWC could involve a number of possible mechanisms that could include, 1- Cd exchange with cations associated MSWC which attributing to co-precipitation inner-sphere complexation with complexed humic matter and mineral oxides of MSWC and 2- physical adsorption and surface precipitation. The increase in electrostatic adsorption of Cd may be attributed to the existence of large amount of negative surface-charge on B600-treated soils. Generally, Fe<sup>0</sup>, MSWC and Mn<sup>0</sup> treatments were superior to the B600, CFA and B300 for stabilizing Cd in desorption experiment.

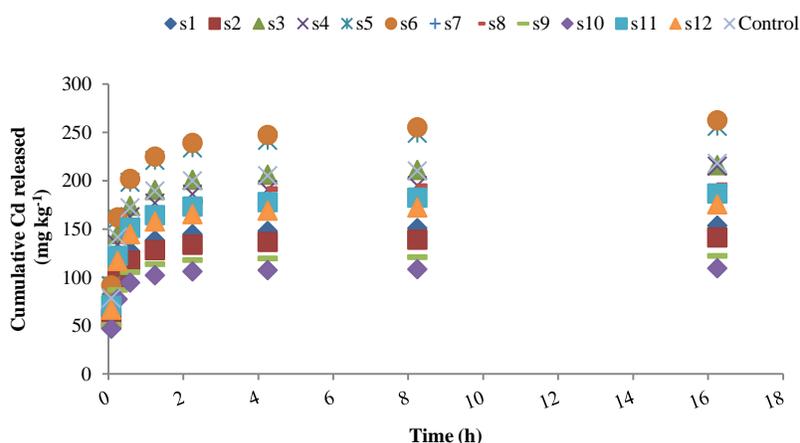


Figure 3. Desorption of Cd by 0.01 M EDTA with time in treated soils.

The two first-order reactions model was used for predicting Cd desorption. This model exhibited two pools for Cd: a “labile” part ( $Q_1$ ), rapidly extracted with a rate constant  $k_1$ , and a “fairly labile” part ( $Q_2$ ), more slowly extracted, with a rate constant  $k_2$  [19]. The parameters of two first-order reactions ( $Q_1$ ,  $K_1$ ,  $Q_2$ ,  $K_2$ ,  $R^2$ , SE, and  $Q_1/Q_2$ ) are presented in Table 5. According to the obtained highest values of the  $R^2$  and lowest values of the SE, two first-order reaction models was able to describe the observed results of Cd release in soil samples. Figure4 shows the experimental extraction rate data and the fitted curves obtained with the two first-order reaction model for six amended soils and control treatment. The rate of  $Q_1$  (quickly extracted) in amended

soils was lower (Except for B300) than control soil, meaning reduction Cd availability due to application amendments. High ratio of  $Q_1/Q_2$  indicated that the labile metal fraction has greater than the less labile fraction. The lower ratio of  $Q_1/Q_2$  of amended soils compared to control treatment confirmed positive effect of amendment to stabilization of Cd. Application amendments increased the rate of  $Q_2$  (slowly extracted) than control soil. The assumption is that the fractions of Cd determined with two first-order reactions model is correlative with fractionation of Cd derived from fractionation method. Hence, simple correlation coefficient ( $r$ ) was estimated for relationships among parameters of the two first-order reactions model and

chemical forms of Cd (Table 6). There was a positive significant correlation between  $Q_1$  with EX and Car,  $Q_2$  with Ex,  $K_2$  with  $K_1$ . On the other hands, there was a negative significant correlation between  $Q_1$  with  $K_1$  and  $K_2$ ,  $K_1$  with EX,  $Q_2$  with Res,  $K_2$  with EX. Jalali and Sajadi Tabar [18] found a significant correlation between  $Q_2$  with Om, inorganic precipitates fraction, and Res fractions of Nickel.  $Q_1$  could be related to Ex fraction and part of Om fraction;  $Q_2$  could be related to the Om residual and inorganic precipitates fraction, and  $Q_3$  could be related to residual fraction [35]. The results of correlation coefficients between chemical forms of Cd and parameters of two first-order reactions model confirmed the hypothesis of Brunori et al. [35] based on positive correlation between  $Q_1$  with mobile fractions (EX and Car).

### CONCLUSIONS

In present study, the effects of six different kinds of amendments on desorption and chemical forms of Cd were tested in a Cd-spiked soil. Stabilization of Cd was determined by measuring desorption and fractionation of Cd in batch-type experiments. The results showed that all amendments (except for B300) reduced Cd

dynamic. Changes in Cd fractions and their conversion into less soluble forms were clear in treated soils. The addition of amendments resulted in a significant reduction in mobility factor of Cd compared to the control treatment. Among all amendments tested,  $Fe^0$  was the most effective treatment in decreasing dynamic of Cd.  $Fe^0$ , MSWC and  $Mn^0$  treatments were superior to the B600, CFA and B300 for stabilizing Cd in desorption experiment. Biphasic pattern of Cd desorption kinetic was fitted well by the model of two first-order reactions. This model exhibited two pools for Cd: a labile part ( $Q_1$ ), rapidly extracted and a fairly labile part ( $Q_2$ ), more slowly extracted. The rate of  $Q_1$  (quickly extracted) in amended soils was lower (Except for B300) than control soil, meaning reduction Cd availability due to application amendments. In general, from the practical of view,  $Fe^0$ , MSWC and  $Mn^0$  treatments are effective in Cd immobilization, while application of  $Fe^0$  at the rate 5% (W/W) was the best treatment for stabilization of Cd from polluted soils. It is recommended that further work will need to achieve insight into their potential synergetic effect.

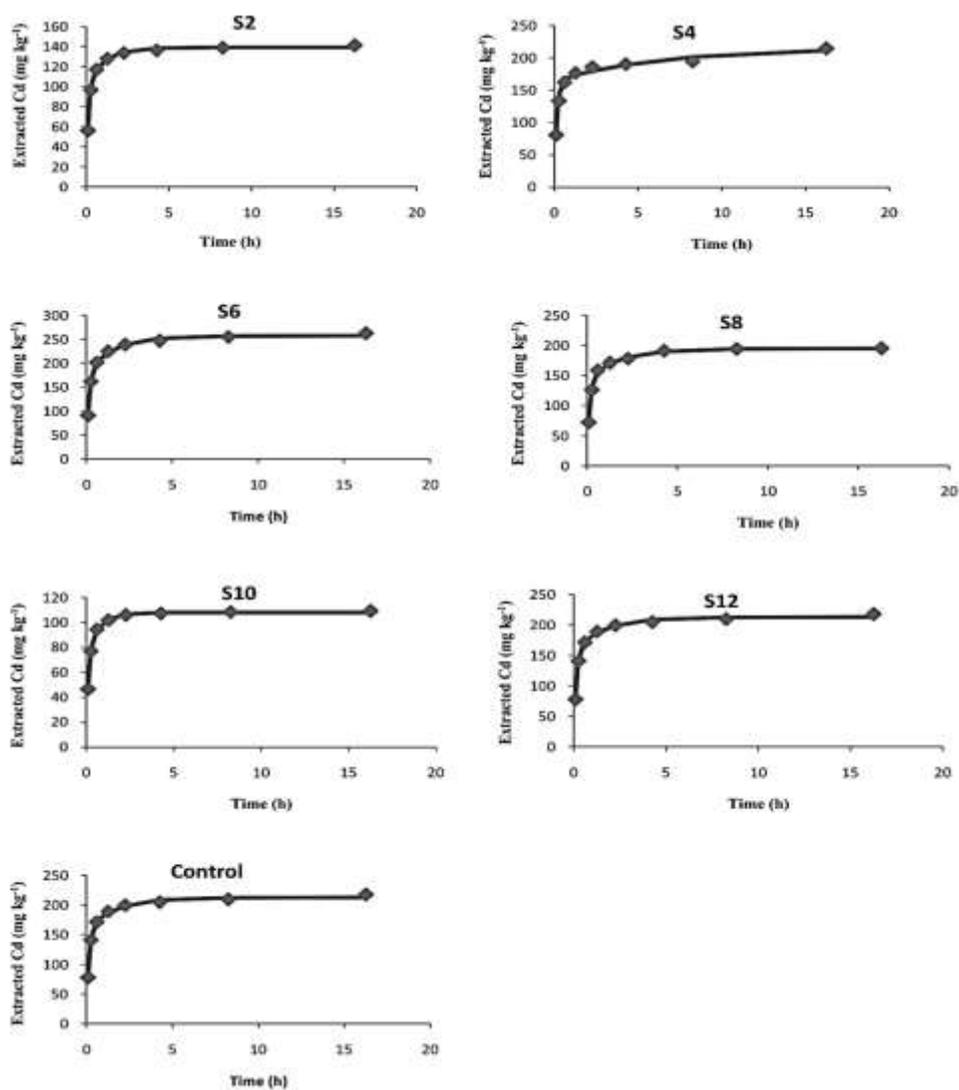
**Table 5.** Estimated parameters of the two first-order reactions model used to describe release kinetics of Cd

Value	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Control
$Q_1$	112.818	102.148	149.530	165.143	177.578	181.296	136.638	145.338	90.651	73.829	136.638	127.445	159.278
$K_1$	8.526	8.783	9.689	7.188	7.818	7.617	7.913	7.510	8.823	10.159	7.913	8.007	7.587
$Q_2$	38.301	37.070	62.413	51.622	73.730	76.444	47.036	49.767	30.142	34.269	47.036	45.357	54.113
$K_2$	0.814	0.898	0.791	0.149	0.629	0.603	0.649	0.542	1.116	1.440	0.649	0.824	0.576
$R^2$	0.998	0.998	0.996	0.985	0.996	0.996	0.997	0.998	0.998	0.998	0.997	0.997	0.996
SE	30.520	31.220	41.920	41.370	54.240	56.300	32.390	41.300	23.900	21.160	38.260	36.190	53.690
$Q_1/Q_2$	2.946	2.756	2.396	3.199	2.408	2.372	2.905	2.920	3.007	2.154	2.905	2.810	2.943

**Table 6.** Simple correlation coefficient between parameters of two first-order reactions and chemical forms of Cd in amended soils

	Q <sub>1</sub>	K <sub>1</sub>	Q <sub>2</sub>	K <sub>2</sub>	Q <sub>1</sub> /Q <sub>2</sub>	EX	Car	Om	Mn-Ox	FeA-Ox
K <sub>1</sub>	-.706**									
Q <sub>2</sub>	.908**	-.410								
K <sub>2</sub>	-.832**	.854**	-.543							
Q <sub>1</sub> /Q <sub>2</sub>	.027	-.576*	-.383	-.511						
EX	.885**	-.742**	.801**	-.752**	.071					
Car	.644*	-.362	.526	-.547	.132	.539				
Om	.443	-.421	.441	-.403	-.040	.718**	.102			
Mn-Ox	.157	.122	.280	.033	-.408	.254	.374	.393		
FeA-Ox	-.381	.279	-.317	.412	-.210	-.556*	-.288	-.528	-.066	
Res	-.484	.195	-.556*	.349	.302	-.548	-.204	-.680*	-.724**	.423

\*Correlation is significant at the 5% level \*\*Correlation is significant at the 1% level.



**Figure 4.** Observed (■) and predicted values (—), as described by two first-order reaction model, of Cd released from the studied soils

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## REFERENCES

1. Alloway B.J., 2013. Heavy Metals and Metalloids as Micronutrients for Plants and Animals. In Heavy Metals in Soils. Springer Netherlands. pp. 195-209.
2. Loganathan P., Vigneswaran S., Kandasamy J., 2013. Road-Deposited Sediment Pollutants: A Critical Review of their Characteristics, Source Apportionment, and Management. Critical Reviews in: Environ Sci Technol. 43(13), 1315-1348.
3. Terzano R., Spagnuolo M., Medici L., Vekemans B., Vincze L., Janssens K., Ruggiero P., 2005. Copper stabilization by zeolite synthesis in polluted soils treated with coal fly ash. Environ Sci Technol. 39, 6280–6287.
4. Hamon R.E., McLaughlin M.J., Cozens G., 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. Environ Sci Technol. 36, 3991-3996.
5. Basta N.T., Gradwohl R., Snethen K.L., Schroder J.L., 2001. Chemical immobilization of lead, zinc, and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J Environ Qual. 30(4), 1222-1230.
6. Chen H.M., Zheng C.R., Tu C., Shen Z.G., 2000. Chemical methods and phytoremediation of soil contaminated with heavy metals. Chemosphere. 41(1-2), 229-234.
7. Krebs R., Gupta K.S., Furrer G., Schulin R., 1998. Solubility and plant uptake of metals with and without liming of sludge-amended soils. J Environ Qual. 27, 18–23.
8. Esfandbod M., 2010. Kinetics of cadmium desorption from some soils of Iran. In 19th World Congress of Soil Science, Soil Solutions for a Changing World, Australia, Brisbane.
9. SadeghKasmaei L., Fekri M., 2014. Pollution and Desorption Kinetics of Heavy Metals at Agricultural Soils in the Southeast of Iran. Commun Soil Sci Plant Anal. 45(11), 1435-1445.
10. Bouyoucos G.J., 1962. Hydrometer method improved for making particle size analysis of soil. Agron J. 54, 464–465. Chapman, H.D., 1965. Cation exchange capacity. In: Black CA, Evans DD, Ensminger LE, White JL, Clark FE, editors. Methods of soil analysis part 2. Chemical and microbiological properties. Monogr. 9. 2nd ed. Madison (WI): Agronomy Society of America and Soil Science Society of America; p. 891–901.
11. Chapman H.D., 1965. Cation exchange capacity. In: Black C.A., Evans D.D., Ensminger L.E., White J.L., Clark F.E., editors. Methods of soil analysis part 2. Chemical and microbiological properties. Monogr. 9. 2nd ed. Madison (WI): Agronomy Society of America and Soil Science Society of America; p. 891–901.
12. Jackson M.L., 1958. Soil chemical analysis. Englewood Cliffs (NJ): Prentice-Hall.
13. Allison L.E., Moodie C.D., 1965. Carbonate. In: Black C.A., Evans D.D., Ensminger L.E., White J.L., Clark F.E., editors. Methods of soil analysis part 2. Chemical and microbiological properties. Monogr. 9. 2nd ed. Madison (WI): Agronomy Society of America and Soil Science Society of America; p. 1379–1396.
14. Lindsay W.L., Norvell W.A., 1978. Development of a DTPA test for zinc, iron, manganese, and copper. Soil Sci Soc Am J. 42, 421–428.
15. Sposito G., Lund L., Chang A., 1983. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. Soil Sci Soc Am J. 46, 260–264.
16. Singh J.P., Karwasra S.P.S., Singh M., 1988. Distribution and forms of copper, iron, manganese, and

- zinc in calcareous soils of India. *Soil Sci.* 146(5), 359-366.
17. Salbu B., Krekling T., 1998. Characterisation of radioactive particles in the environment. *Analyst*, 123(5), 843-850.
18. Jalali M., SajadiTabar S., 2013. Kinetic extractions of nickel and lead from some contaminated calcareous soils. *Soil Sediment Contam.* 22(1), 56-71.
19. Santos S., Costa C.A., Duarte A.C., Scherer H.W., Schneider R.J., Esteves V.I., Santos E.B., 2010. Influence of different organic amendments on the potential availability of metals from soil: A study on metal fractionation and extraction kinetics by EDTA. *Chemosphere.* 78(4), 389-396.
20. Rajaei M., Karimian N., Maftoun M., Yasrebi J., Assad M.T., 2006. Chemical forms of cadmium in two calcareous soil textural classes as affected by application of cadmium-enriched compost and incubation time. *Geoderma.* 136, 533-541.
21. Khanmirzaei A., Bazargan K., Amir Moezzi A., Richards B.K., Shahbazi K., 2013. Single and sequential extraction of cadmium in some highly calcareous soils of Southwestern Iran. *J soil sci plant nutr.* 13(1), 153-164.
22. Houben D., Pircar J., Sonnet P., 2012. Heavy metal immobilization by cost-effective amendments in a contaminated soil: effects on metal leaching and phytoavailability. *J GeochemExplor.* 123, 87-94.
23. Naidu R., Bolan N.S., Kookana R.S., Tiller K.G., 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Eur J Soil Sci.* 45(4), 419-429.
24. Watanabe T., Murata Y., Nakamura T., Sakai Y., Osaki M., 2009. Effect of zero-valent iron application on cadmium uptake in rice plants grown in cadmium-contaminated soils. *J Plant Nutr.* 32(7), 1164-1172.
25. Aboulroos S.A., Helal M.I.D., Kamel M.M., 2006. Remediation of Pb and Cd polluted soils using in situ immobilization and phytoextraction techniques. *Soil Sediment Contam.* 15(2), 199-215.
26. Jiang J., Xu R.K., Jiang T.Y., Li Z., 2012. Immobilization of Cu (II), Pb (II) and Cd (II) by the addition of rice straw derived biochar to a simulated polluted Ultisol. *J Hazard Mater.* 229, 145-150.
27. Lee S.H., Lee J.S., Jeong Choi Y., Kim J.G. 2009. In situ stabilization of cadmium-, lead-, and zinc-contaminated soil using various amendments. *Chemosphere.* 77(8), 1069-1075.
28. Vaca-Paulin R., Esteller-Alberich M.V., Lugo-De La Fuente J., Zavaleta-Mancera H.A., 2006. Effect of sewage sludge or compost on the sorption and distribution of copper and cadmium in soil. *Waste Manag.* 26(1), 71-81.
29. Knox A.S., Adriano D.C., 2002. Evaluation of Sequestering Agents for Cadmium Contaminated Soils. *Environmental Science and Technology.* Uzouchukwu G.A., Schimmel K., Reddy G.B., Chang S., Kabadi V. (Eds). Battelle Press, Richland. 205-213.
30. Houben D., Sonnet P., 2010. Leaching and phytoavailability of zinc and cadmium in a contaminated soil treated with zero-valent iron. In *Proceedings of the 19th World Congress of soil science, soil solutions for a changing World* (pp. 1-6).
31. Kirpichtchikova T.A., Manceau A., Spadini L., Panfili F., Marcus M.A., Jacquet T., 2006. Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochim Cosmochim Ac.* 70(9), 2163-2190.
32. Mayel S., Ghasemi-Fasaei R., Karimian N., Ronaghi A., Zarei M., Jarrah M., 2014. Desorption behaviour of lead in two calcareous soils as affected by Pb level without and with compost supply. *Arch Agron Soil Scie.* 60(2), 265-274.
33. Friesl W., Horak O., Wenzel W.W., 2004. Immobilization of heavy metals in soils by the application of bauxite residues: pot experiments under field conditions. *J Plant Nutr Soil Sci.* 167(1), 54-59.

34. Shuman L.M., Dudka S., Das K., 2002. Cadmium forms and plant availability in compost-amended soil. *Commun Soil Sci Plant Anal.* 33(5-6), 737-748.
35. Brunori C., Cremisini C., D'annibale L., Massanisso P., Pinto V., 2005. A kinetic study of trace element leach ability from abandoned-mine-polluted soil treated with SS-MSW compost and red mud. Comparison with results from sequential extraction. *Anal Bio anal Chem.* 381(7), 1347-1354.

