Int. J. Environ. Sci. Technol. (2018) 15:2433–2446
https://doi.org/10.1007/s13762-017-1544-3

ORIGINAL PAPER

Investigation of cadmium immobilization in a contaminated calcareous soil as influenced by biochars and natural zeolite application

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Received: 5 April 2017 / Revised: 31 July 2017 / Accepted: 10 September 2017 / Published online: 20 September 2017
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Abstract The effect of natural zeolite and biochars addition on the immobilization of cadmium in a calcareous soil was investigated using a combined factorial experiment under laboratory conditions. The following factors were evaluated: zeolite applied at 0, 3 and 6% (w/w) in combination with five different biochars at 3% (w/w), namely wheat straw biochar, corn straw biochar, licorice root pulp biochar, rice husk biochar and sheep manure biochar. Two different methods including a sequential extraction procedure and desorption kinetic experiment (using 0.01M EDTA) were used to assess the effectiveness of applied treatments for cadmium stabilization in soil. It was observed that with increasing the levels of zeolite application from 0 to 6%, the concentration of water-soluble plus exchangeable, carbonate-bound, Fe–Mn-oxide-bound and organic-bound fractions was significantly reduced, while the residual content of cadmium was increased. Changes in chemical fractions of cadmium and their transformation into more stable forms were also observed with application of all biochars. Use of all amendments led to a significant decrease in cadmium desorption during 48 h compared to the control soil, with sheep manure biochar + 6% zeolite combined treatment being the most effective. This was mainly attributed to the high-lime, P and O + S functional group content of the sheep manure biochar and the high pH and CEC of the natural zeolite. Ultimately, it was concluded that addition of sheep manure biochar + 6% zeolite combined treatment was best for enhancing the immobilization of cadmium in the contaminated calcareous soil.

Editorial responsibility: Hari Pant.

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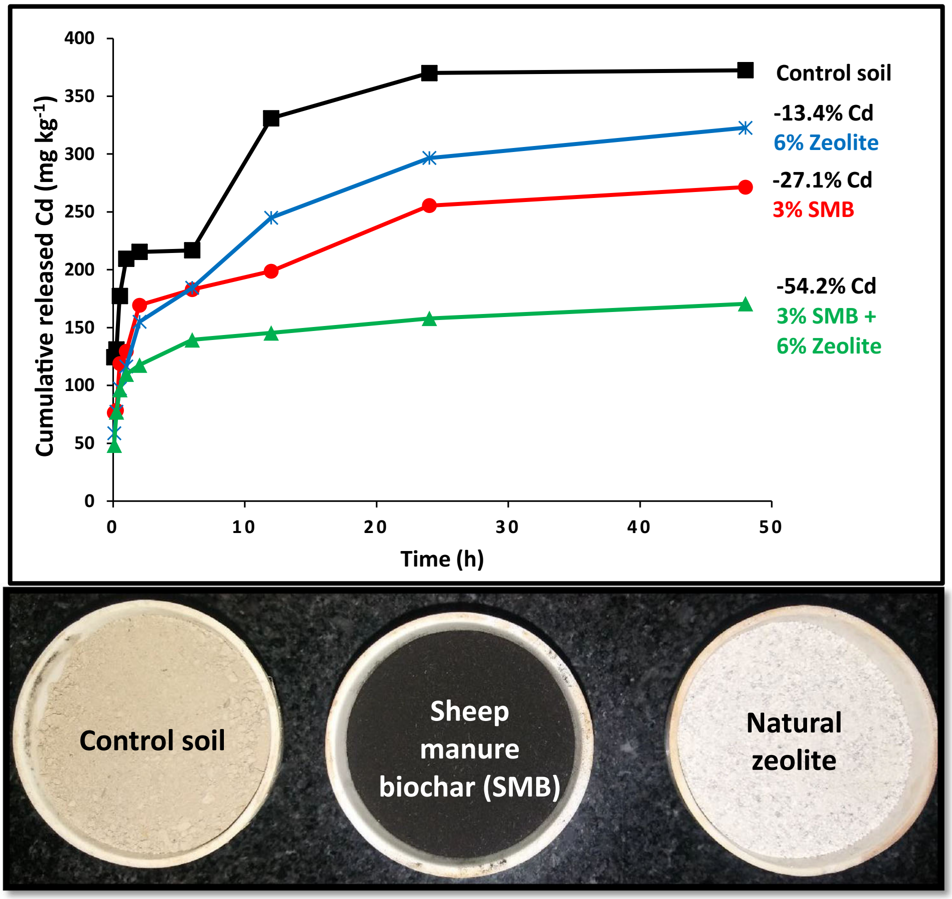
Graphical Abstract



Keywords Stabilization · Desorption · Chemical forms · Functional group · Cation exchange capacity

Introduction

Under natural conditions, concentrations of heavy metals, especially cadmium (Cd), are low in soils, except in those derived from shales (Alloway and Jackson 1991). Considerable amount of Cd can be introduced into soils via anthropogenic pathways such as dumping industrial effluents, agricultural application of sewage sludge (Duquet and Vedy 1991; Jamali et al. 2009; Sahito et al. 2015) and the addition of commercial fertilizers (Singh 1994). Cadmium is known to be more mobile and soluble than many other heavy metals in soil. The limit of Cd concentration in soil associated to biomass reduction for the majority of agricultural plants is reported to be between 5 and 15 mg Cd kg^{-1} of soil (Li et al. 2001).

A range of effective physical and chemical remediation strategies exist for metal contaminated soils, but most of them are expensive and would be more ideal for relatively small-scale contaminated sites (Debela et al. 2012). One promising remediation technique is the in situ stabilization whereby an amendment is incorporated into a contaminated soil in order to immobilize heavy metals and reduce the dose(s) received by plants (receptors) without set-aside effects (Hosseini et al. 2013). This technique decreases the hazard potential of the contaminated soil by converting the contaminants into their least soluble or toxic form (Karbassim et al. 2014). Amendments may bind, adsorb or co-precipitate metal contaminants, reducing their mobility and availability.

Biochar (BC) is the solid product of pyrolysis, designed to be used for environmental remediation (Lehmann and Joseph 2015). Due to its high aromaticity, BC is considered as a strong and effective sorbent for both organic and inorganic pollutants (Bian et al. 2013). The functional groups of BC influence the sorption process depending on the nature of their surface charge so that both transition metals and non-transition metals can be sorbed onto the surface of BC particles (Amonette and Joseph 2009).

Several kinds of biomass can serve as source materials of BC, for example, woodchips, animal manure and crop residues (Tang et al. 2013). The heavy metals retained by BC will be released at a slower rate than if other organic materials are used, which decompose more rapidly (Tang et al. 2013). In recent years, natural substances such as zeolite (clay) have been used to adsorb heavy metals from soil to decrease their availability to plants (Inglezakis et al. 2002). Zeolite is a natural mineral that has been studied extensively for its remediation potentiality of hazardous heavy metal-polluted soils (Shanableh and Kharabsheh 1996). Compared to other stabilization materials, zeolite application is fast, clean and inexpensive (Mahabadi et al. 2007).

Different procedures were used to determine the efficiency of various amendments in stabilization of heavy metals in contaminated soils, such as sequential extraction method, leaching test and adsorption–desorption experiments. The mobility of heavy metals is controlled by the sorption and desorption characteristics of soil (Krishnamurti et al. 1999). Desorption of heavy metals from soil can be related to their mobility and toxicity (Violante and Krishnamurti 2007). In addition, sequential extraction procedures such as that developed by Tessier et al. (1979) or Shuman (1985) can be suitable in tracing the stabilization process of heavy metals in contaminated soil especially when amendments (such as biochar, compost and manure) were added to the soil. These procedures estimate the distribution of heavy metals among the water-soluble plus exchangeable (WSEX), carbonate (CARB), Fe–Mn-oxide (FeMnOX), organic (OM), and residual (RES) fractions. Water-soluble plus exchangeable fraction is regarded as a mobile pool of heavy metals, while others fractions are less mobile in soil (Ma and Rao 1997). Mahabadi et al. (2007) demonstrated that the addition of natural zeolite to a Cd-contaminated soil efficiently reduced Cd mobility and increased its stabilization capacity, using a leaching experiment. It was related to the high pH (9.10) and CEC (1.40 meq g^{-1}) of applied zeolite. Mirzaei et al. (2013) reported that the addition of zeolite to the contaminated soil column reduced the concentration of heavy metals (Cd, Pb, Ni and Cr) in the effluent. Also Lucchinia et al. (2014) reported that the repeat application of wood-derived biochar (*Fagus sylvatyca* L. pyrolyzed at 550 °C) (25 t ha^{-1}) to a Cd-contaminated soil increased the proportion of Cd residual fraction and reduced carbonate-bound fraction. Furthermore, Mohammad et al. (2015) found that the addition of conocarpus biochar (0, 1, 3 and 5% w/w) as a soil amendment significantly reduced ammonium bicarbonate-DTPA extractable of Zn, Cu and Cd concentrations of contaminated soil, indicating metal immobilization.

The objectives of present work were (1) to examine the influence of biochars (derived from different organic wastes), natural zeolite levels and their combination on the transformation of the chemical forms of Cd, (2) to evaluate the release of Cd as affected by biochar and natural zeolite (both independently and in combination) application and (3) to assess the ability of these soil amendments to reduce the mobility of Cd using a sequential extraction procedure and kinetic data obtained from 0.01M EDTA in an artificially contaminated soil. This research was conducted at the beginning of 2016 at the college of agriculture and natural resources of Darab, Shiraz University, Iran.

Materials and methods

Soil sampling and characteristics

An uncontaminated soil sample (about 20 kg) was compositely collected from the surface layer (0–20 cm depth) of a calcareous soil (Coarse-loamy, carbonatic, hyperthermic Typic Haplustepts) from the agricultural field of the college of agriculture and natural resources of Darab, Shiraz University at Darab district about 260 km southeastern of Shiraz, Iran. The sample was air-dried for 1 week, thoroughly mixed and passed through a 2-mm mesh sieve. Routine soil analysis was performed to determine soil texture by hydrometer method (Gee and Or 2002); pH of saturated paste (Thomas 1996); electrical conductivity (EC_e) of saturation extract (Rhoades 1996); organic carbon (OC) by oxidation with chromic acid and titration with ferrous ammonium sulfate (Nelson and Sommers 1996); calcium carbonate equivalent (CCE) by neutralization with hydrochloric acid and titration with sodium hydroxide (Loeppert and Suarez 1996); available phosphorous (P) by extracting with sodium bicarbonate (Kuo 1996), available zinc, copper, manganese and iron by extracting them with diethylene triamine pentaacetic acid, DTPA (Loeppert and Inskeep 1996), and determining their elemental concentrations by spectrophotometry and atomic absorption (PG 990, PG Instruments Ltd. UK), respectively. Also, total concentration of Cd in the soil was determined in filtered extracts obtained from 2.0-g samples, which were digested overnight with 12.5 mL 4M nitric acid (HNO_3) at 80 °C (Amacher 1996). The selected properties of the calcareous topsoil are shown in Table 1.

Biochars production and characteristics

The biochars used in this study were obtained from five organic wastes (corn straw, wheat straw, rice husk, licorice root pulp and sheep manure) through a slow pyrolysis process. The biomasses were air-dried for 1 week and then oven-dried at 80 °C for 2 days. Each biomass sample was crushed to <1.0 mm particle size using a mechanical

Table 1 Selected physicochemical properties of the calcareous topsoil

Property	Value	Property	Value
Soil textural class	Loam	Available-P (mg kg^{-1})	15.0
pH_s	7.60	DTPA-zinc (mg kg^{-1})	0.80
Electrical conductivity (dS m^{-1})	0.90	DTPA-copper (mg kg^{-1})	1.50
Soil organic matter (%)	1.20	DTPA-manganese (mg kg^{-1})	12.6
Cation exchange capacity ($cmol_c$ kg^{-1})	17.3	DTPA-iron (mg kg^{-1})	5.30
Calcium carbonate equivalent (%)	52.0	Total cadmium (mg kg^{-1})	Trace

Table 2 Chemical characteristics of applied biochars

Property	Corn straw biochar	Wheat straw biochar	Licorice root pulp biochar	Rice husk biochar	Sheep manure biochar
EC (1:10) (dS m^{-1})	5.14	11.6	2.40	1.82	9.96
pH (1:20)	10.6	10.5	9.50	11.0	10.2
Total C (%)	68.0	56.2	57.8	49.2	31.8
Total H (%)	2.84	2.48	2.25	2.19	1.00
Total N (%)	1.24	0.71	2.43	0.77	0.90
Total P (%)	0.30	0.04	0.06	0.09	0.25
Total Cd (mg kg^{-1})	3.60	2.20	6.70	1.90	6.70
Ash content (%)	20.6	31.7	29.7	37.8	52.7
O + S content (%)[a]	5.13	7.34	6.21	8.70	12.9
H/C mole ratio	0.50	0.61	0.47	0.53	0.38

[a] Determined by subtraction of ash, moisture, C, N and H from total mass

grinder. Then, the powdered biomass was pyrolyzed in a muffle furnace (Shimifan, F47) under limited oxygen condition at temperature of 500 °C. The pyrolysis temperature was raised gradually, starting from room temperature, and increased by 5 °C per min to reach 500 °C (the final temperature) which was held constant for 4 h for slow pyrolysis; then, the biochar was allowed to cool and ground once again to pass through a 0.5-mm sieve prior to use (Melo et al. 2013).

Basic chemical parameters of produced biochars were determined in the following way. The pH value of biochar samples was determined using published method (Sun et al. 2014). Briefly, 1.0 g of sample was added to 20 mL DI water. The suspension was shaken with a mechanic shaker at 40 rpm for 1 h and equilibrated for 5 min before measuring pH with a pH meter. The electrical conductivity (EC) was measured using a 1:10 biochar/DI water ratio after shaking for 30 min at 25 °C (Yang et al. 2015). The percentage of carbon, nitrogen and hydrogen of biochar was determined by the CHN analyzer (ThermoFinnigan Flash EA 1112 Series). Cation exchange capacity (CEC) was measured by using ammonium acetate method (Abdelhafez et al. 2014). Briefly, 20 mL of NH_4OAC (1M) at pH 7.0 was added to 4 g of biochar sample and the mixture was shaken for 1 h, filtered through Whatman 42 filter paper, and finally then concentration of Ca, Mg, Na and K was measured in the filtrate. Total Cd was determined using atomic absorption (PG 990, PG Instruments Ltd. UK) after ashing at 550 °C and acid dissolution (Ding et al. 2015). Total P was determined in the acid-digested ash fraction using the molybdate-ascorbic acid procedure by spectrophotometry at 460 nm wave length (Lu 1999). The chemical characteristics of the biochars used in this experiment are listed in Table 2. The functional groups of the biochars were characterized using FTIR (KBr pellet method) spectroscopy (Shimadzu DR-8001).

Table 3 Elemental composition of the natural zeolite (%)

Cl	TiO_2	MgO	CaO	K_2O	Na_2O	Fe_2O_3	Al_2O_3	SiO_2
0.77	0.13	0.41	0.27	2.13	3.56	0.59	8.47	70.6

Zeolite characteristics

The natural zeolite used in this study originated from the mines of Semnan province, Iran. The sample was ground and passed through a 0.5-mm sieve. The CEC value of this sample was 81 $cmol_c$ kg^{-1}, and its pH was approximately 10.0 (1:10 solid/water). Table 3 summarizes the elemental composition of the zeolite powder used in the experiment.

Table 4 Cadmium sequential extraction procedure

Fractions	Reagent	Agitation time
Water soluble plus exchangeable (WSEX)	20 mL of 1 M NH_4OAc (pH 7)	2 h
Carbonate bound (CARB)	20 mL of 1 M NH_4OAc (pH 5)	2 h
Fe–Mn-oxide bound (FeMnOX)	20 mL of 0.04 M NH_2OH. HCl in 25% (v/v) CH_3COOH	6 h at 60 °C
Organic bound (OM)	15 mL of 30% (v/v) H_2O_2 (pH 2, HNO_3)	5.5 h at 80 °C (on water bath)
	and After cooling, 5 mL of 3.2 M NH_4OAc in 20% (v/v) HNO_3	30 min
Residual (RES)	Calculated by subtracting the sum of four fractions from total Cd (Kamali et al. 2011)	

Experimental design and statistical analysis

A combined factorial experiment as completely randomized design was set up with three replications. Factors included three zeolite levels (0% (Z_0), 3% (Z_1) and 6% (Z_2) (w/w)), and five different biochars applied at 3% (w/w), namely rice husk biochar (RHB), wheat straw biochar (WSB), sheep manure biochar (SMB), corn straw biochar (CSB) and licorice root pulp biochar (LRB) and control (C) with no biochar. Statistical analysis of data was done using MSTATC package (Mstatc 1991). Comparison between means was performed using Duncan's multiple range test (DMRT) at the significant level of $P < 0.05$. Also, the statistical correlation tests were done by SPSS 15.0 computer package.

Soil preparation and incubation experiment

The air-dried soil (200 g) was mixed with aqueous solution containing 500 mg Cd^{2+} per kg of soil, which was prepared by dissolving $Cd(NO_3)_2·4H_2O$ into deionized water (Saffari et al. 2015). The treated soil was thoroughly mixed and placed at 25 ± 2 °C to dry. The samples were ground, and water added until the moisture reached the field capacity level. The wetting and air-drying cycle procedure was repeated five times to allow sufficient mixing of cadmium and soil to simulate actual field conditions (Mahabadi et al. 2007; Lin et al. 1998). The contaminated soil samples were thoroughly mixed with the zeolite and biochars based on the experimental design. Distilled water was added to soil by volume until the soil moisture content reached about the field capacity level and was maintained throughout the incubation period by periodically weighing the plastic containers. The sealed containers were incubated at room temperature (22 ± 2 °C) for 90 days. After incubation, the soil samples were air-dried for 72 h, sieved and kept for chemical analysis.

Sequential extraction procedure

Soil Cd was fractionated into five fractions using the method of Salbu et al. (1998) Table 4 provides an outline of the Salbu et al. (1998) fractionation procedure. Cadmium mobility was evaluated using a mobility factor (Salbu et al. 1998) and calculated according to the following equation (Eq. 1):

$$[(\mathrm{WSEX} + \mathrm{CARB})/\text{sum of five fractions}] \times 100. \qquad (1)$$

Desorption kinetic model

For Cd desorption studies, 5 g of the air-dried <2-mm soil fraction was extracted with 25 mL of 0.01M EDTA at pH 7.0 (Dang et al. 1994) on an end-over-end circulatory shaker for periods of 0.083–48 h (0.083, 0.25, 0.50, 1, 2, 6, 12, 24 and 48 h) at 25 ± 2 °C and then centrifuged immediately at 3000 rpm for 15 min. The supernatants were filtered through Whatman 42 filter paper, and Cd concentration was determined using AAS (PG 990, PG Instruments Ltd. UK). Cumulative Cd released (q) as a function of time (t) was evaluated using seven different kinetic models (Table 5). A relatively high values of coefficient of determination (r^2) and low values of standard error of estimate (SE) were used as criteria for the selection of the best fitted models. Standard errors of estimate were calculated as follows (Eq. 2):

$$\mathrm{SE} = \left[\Sigma\,(q - q*)^2/(n-2)\right] \qquad (2)$$

where q and $q*$ represent the measured and predicted Cd released, respectively, and n is the number of observations. Various Cd release rate parameters were subsequently obtained from fitted equations.

Table 5 Kinetic models used to describe time (t) dependent cumulative amount of Cd release (q_t) from soil

Models	Equations	Parameters
Zero order (Sparks 2011)	$q_t = q_o - k_o t$	k_o, zero-order rate constant (mg Cd kg^{-1} s^{-1})
First order (Sparks 2011)	$Ln\, q_t = Lnq_0 - k_1 t$	k_1, first-order rate constant (s^{-1})
Second order (Sparks 2011)	$1/q_t = 1/q_o - k_2 t$	k_2, second-order rate constant [(mg Cd kg^{-1})$^{-1}$]
Third order (Sparks 2011)	$1/q_t = 1/q_0^2 - k_3 t$	k$_3$, third-order rate constant [(mg Cd kg^{-1})$^{-2}$]
Parabolic diffusion (Sparks 2011)	$q_t = q_o + k_p t^{0.5}$	K_p, diffusion rate constant (mg Cd kg^{-1} h$^{-0.5}$)
Power function (Sparks 2011)	$q_t = at^b$	a, initial Cd desorption rate constant (mg Cd kg^{-1} h^{-1})^b and b, desorption rate coefficient [(mg Cd kg^{-1})$^{-1}$]
Simple Elovich (Sparks 2011)	$q_t = a_e + 1/\beta \ln t$	a_e, initial Cd release rate constant (mg Cd kg^{-1}) $1/\beta$, Cd release rate coefficient (mg Cd kg^{-1} h^{-1})

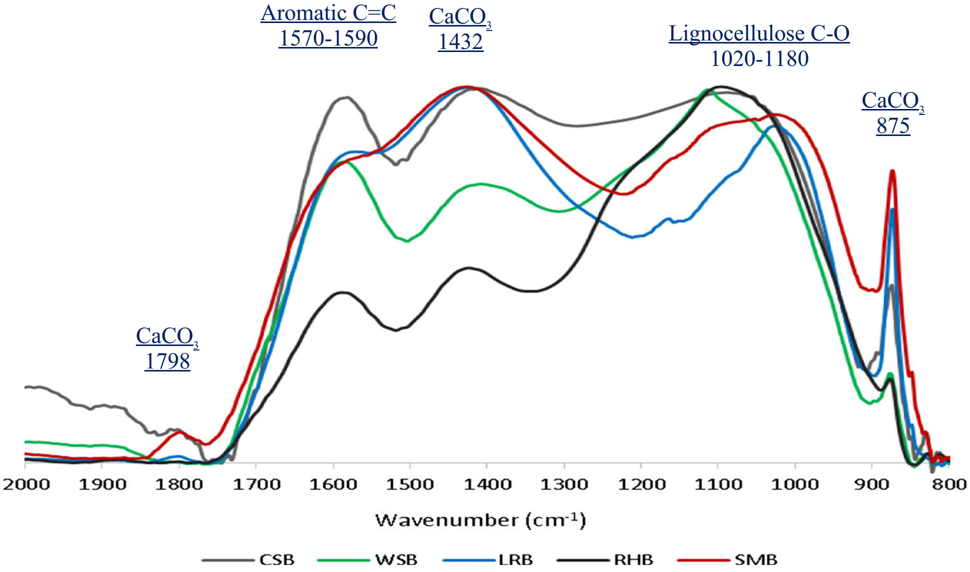


Fig. 1 Comparison of normalized FTIR absorbance spectra (800–2000 cm^{-1}) of biochars used in the study

Results and discussion

Characteristics of biochars

FTIR analysis

The following bands were observed in all of the studied biochars. The broad band around 3400 cm^{-1} was assigned to the presence of –OH groups of alcohols, phenols or carboxyl functional groups (Kieluweit et al. 2010). The weak peaks at around 2870, 2930 and 3030 cm^{-1} were related to symmetric and anti-symmetric stretching vibrations of CH$_2$ in alkanes (Kieluweit et al. 2010; Larkin 2011). The strong absorption bands at 1570–1590 cm^{-1} could be attributed to the stretching vibration of C=C in aromatic rings (Kieluweit et al. 2010). The strong peaks around 1432 cm^{-1} and sharp peak around 875 cm^{-1} could be assigned to CaCO$_3$ (Bruckman and Wriessnig 2013). The broad peaks at around 1410–1420 cm^{-1} correspond to symmetric C=O stretches of deprotonated carboxyl groups (Lin-Vie et al. 1991) and the bending vibration of CH$_2$ (Larkin 2011). The strong broad bands at around 1180–1020 cm^{-1} are typical for C–O bonds associated with lignocellulose (Kieluweit et al. 2010; Chen et al. 2008). The small peaks at 2512 and 1798 cm^{-1} most visible in CSB, SMB and LRB are also attributed to CaCO$_3$ (Bruckman and Wriessnig 2013).

Comparison of the biochar spectra in the 800–2000 cm^{-1} wavenumber range (Fig. 1) shows that the SMB, LRB and CSB contain the highest amounts of CaCO$_3$ as indicated by the prominent peaks at 875, 1432 and 1798 cm^{-1} (Bruckman and Wriessnig 2013). This would indicate that SMB, LRB and CSB have the greatest liming potential among the biochars. The FTIR spectra also show that the RHB and WSB are dominated by lignocellulose compared to the other biochars as indicated by their most prominent absorbance bands at around

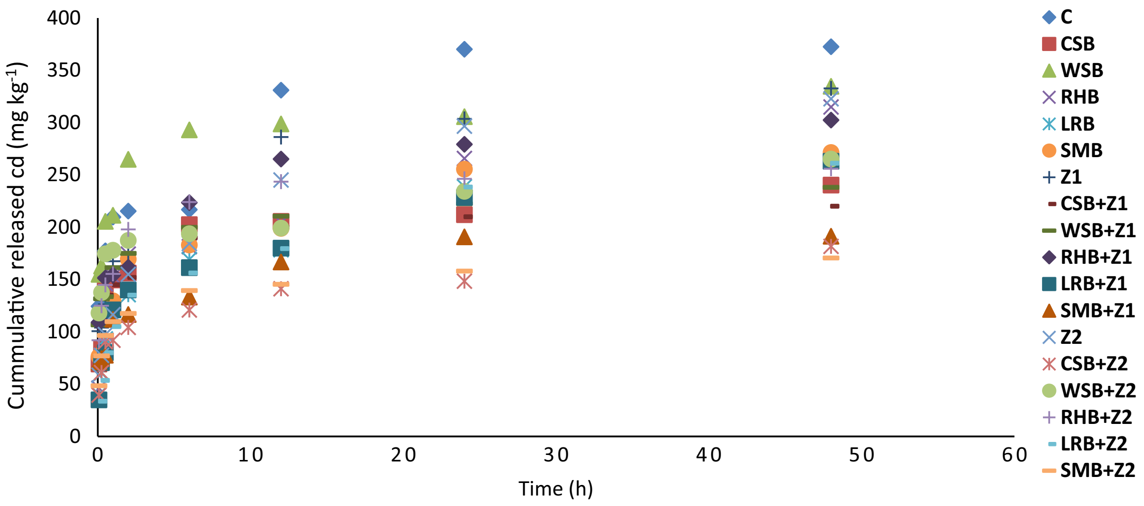


Fig. 2 Cd release pattern as influenced by applied treatments

1100 cm^{-1} (Fig. 1; Chen et al. 2008). Concomitantly, the WSB and especially the RHB contain less aromatic C=C functional groups, as indicated by the relatively weaker peaks at 1585–1588 cm^{-1} (Fig. 1) (Kieluweit et al. 2010; Chen et al. 2008). This could indicate that the WSB and RHB are less carbonized than the other biochars, which is also confirmed by the higher H/C mole ratios of these biochars (Table 2). The lignocellulose C–O (1180–1020 cm^{-1}) and aromatic C=C (1570–1590 cm^{-1}) peaks occur relatively at similar intensities in the CSB, LRB and SMB biochars (Fig. 2) which indicate that they are more aromatic and condensed in nature, as also demonstrated by their lower H/C ratios (Table 2).

Chemical characteristics

The C content of the biochars ranged between 31.8 and 68.0% (Table 2). According to the European Biochar Commission (EBC 2012), for a material to be categorized as a biochar it should contain a minimum of 50.0% C. Therefore, all of the plant material-derived chars (CSB, WSB, LRB and RHB) can be categorized as biochars, whereas the animal waste-derived biochar (SMB) should rather be categorized as pyrogenic carbonaceous material (EBC 2012). Animal waste usually contains a significantly higher proportion of inorganic materials (ash content), thus resulting in much lower C contents (Ro et al. 2010). Indeed the SMB contained the highest ash content of the biochars (52.0%) (Table 2). The more herbaceous the plant feedstock is, the lower the C content of the resultant biochar usually is (Jindo et al. 2014). This would explain the higher C content of the CSB (68.0%) compared to the LRB (57.7%), WSB (56.3%) and RHB (49.2%), as maize residues are relatively woodier than the other plant materials. The O + S content of the biochars varied between 5.13 and 12.89%, with SMB containing the highest O + S content (Table 2).

The H/C mole ratio of chars gives an indication of the aromaticity of the biochar and its degree of carbonization (Krull et al. 2009). According to the EBC (2012) and International Biochar Initiative (IBI), maximum allowable H/C ratio for a material to be categorized as biochar is 0.70. All of the biochars used in this study contained H/C ratios less than 0.70 (Table 2) and thus can be considered as carbonized to a sufficient degree to be considered biochars. The WSB had the highest H/C ratio (0.61), whereas the SMB had the lowest (0.38); this indicates that the SMB was the most carbonized while the WSB was the least.

The EC of the biochars gives an indication of the water-soluble salts, carbonates, oxides and hydroxides present in the biochars. The EC of biochars varied widely, ranging between 1.82 and 11.6 dS m^{-1} (Table 2). The WSB and SMB had the highest EC values (11.6 and 9.96 dS m^{-1}, resp.), whereas the LRB and RHB had the lowest EC values (2.40 and 1.82 dS m^{-1}, resp.). All biochars had alkaline pH, ranging between 9.50 and 11.0 (Table 2). The RHB had the highest pH while (11.0), while the LRB had the lowest (9.50). The measured pH of biochars indicates the net equilibrium reaction between surface acidic and alkaline functional groups and solubility of basic carbonates, hydroxides or oxides in the biochar (Amonette and Joseph 2009). Thus, the pH of biochars measured in water is not a good indicator of the actual liming potential of biochars (Chen et al. 2008). The N (%) of biochars ranged between 0.71 and 2.43% (Table 2). The Cd (mg kg^{-1}) and P (%) contents in biochars were in the range of 2.20–6.70 and 0.04–0.30, respectively (Table 2). The SMB and CSB contained the highest P content (0.25 and 0.30%, resp.) among the biochars.

Effects of amendments on Cd chemical fractions and mobility factor

The sequence of relative percentage of Cd chemical forms in all treatments were as: CARB (39.7–47.5) > RES (24.0–40.7) > FeMnOX (13.3–20.7) > WSEX (4.07–5.25) > OM (1.09–2.89). The CARB fraction formed a major portion of the total soil Cd (Table 5). Khanmirzaei et al. (2013) also found that the CARB fraction (40.0–44.0%) was the dominant Cd chemical form in highly calcareous soils of southwestern Iran. Likewise, Rajaei et al. (2006) reported that the concentration of CARB fraction was higher than other fractions of Cd in calcareous and alkaline soils of Iran amended with cadmium-enriched compost. The high CARB fraction of Cd compared to other forms can be attributed to the high Ca carbonate equivalent content (52.0%) in the studied soil (Table 1). Among the Cd chemical fractions, the OM and WSEX forms had the lowest relative percentage of Cd forms which is probably due to low soil organic matter (1.20%) and high pH (7.60) of tested soil (Table 1). These results are in agreement with the findings of Saffari et al. (2015).

The analysis of variance indicated that the main effects of biochar and zeolite treatments and also their combined effects on the concentration of Cd chemical fractions (except the WSEX fraction, where only main effects were significant) and Cd mobility factor were significant ($P < 0.05$). The mean comparison of main effects of zeolite treatment showed that with increasing the application of zeolite levels from Z_0 to Z_2, the concentration of WSEX, CARB, FeMnOX and OM fractions of Cd was significantly decreased by 10.0, 9.40, 18.7 and 36.2%, respectively, while the concentration of RES form was significantly increased from 144 mg kg^{-1} in Z_0 to 193 mg kg^{-1} (33.6%) in Z_2 (Table 6). According to the results, natural zeolite immobilized Cd in soil by enhancing the concentration of RES form and decreasing the more available fractions (FeMnOX, OM, CARB and WSEX). Mohammadi et al. (2011) reported that the application of zeolite (10.0% w/w) in a Cd-spiked soil decreased the Cd concentration in CARB fraction, while the concentration of RES form of Cd was increased significantly. In addition, the concentration of OM and FeMnOX fractions of Cd showed no significant change. Xiong et al. (2015) indicated

Table 6 Effect of biochar and zeolite levels on Cd (mg kg^{-1}) chemical forms in a Cd-polluted calcareous soil

Treatment	C	CSB	WSB	RHB	LRB	SMB	
WSEX							
Z_0	25.3^{a}	24.1^{bc}	24.4^{a-c}	25.1^{ab}	24.0^{cd}	23.8^{c-f}	24.5^{A}
Z_1	23.5^{e-g}	22.8^{fg}	23.7^{c-f}	23.9^{c-e}	22.9^{e-g}	23.0^{d-g}	23.3^{B}
Z_2	22.9^{d-g}	21.7^{h}	22.8^{e-g}	22.6^{g}	21.1^{h}	20.9^{h}	22.0^{C}
	23.9^{A}	22.8^{B}	23.6^{A}	23.9^{A}	22.7^{B}	22.6^{B}	
CARB							
Z_0	239^{a}	237^{b}	235^{c}	230^{e}	236^{bc}	233^{d}	235 A
Z_1	230^{e}	221^{h}	231^{e}	225^{f}	231^{e}	221^{gh}	226 B
Z_2	211^{j}	217^{i}	206^{k}	216^{i}	223^{g}	204^{l}	213 C
	227^{B}	225^{C}	224^{CD}	223^{D}	230^{A}	219^{E}	
FeMnOX							
Z_0	103^{a}	84.6^{d}	86.8 d	86.2^{d}	90.7^{c}	94.2^{b}	91.0^{A}
Z_1	90.0^{c}	79.7^{fg}	82.7^{e}	81.8^{ef}	82.1^{e}	87.1^{d}	83.9^{B}
Z_2	78.6^{g}	68.5^{i}	69.7^{i}	73.9^{h}	75.1^{h}	78.2^{g}	74.0^{C}
	90.55^{A}	77.72^{E}	79.7^{D}	80.6^{D}	82.7^{C}	86.5^{B}	
OM							
Z_0	12.5^{b}	10.3^{c}	9.73^{d}	8.35^{e}	7.70^{fg}	14.4^{a}	10.5^{A}
Z_1	7.54^{g-i}	8.02^{ef}	7.63^{f-h}	7.46^{g-i}	7.10^{i-k}	8.16^{e}	7.65^{B}
Z_2	7.19^{h-j}	6.86^{jk}	6.66^{k}	6.11^{l}	5.93^{l}	7.39^{g-i}	6.69^{C}
	9.08^{B}	8.39^{C}	8.00^{D}	7.30^{E}	6.91^{F}	9.97^{A}	
RES							
Z_0	125^{k}	150^{i}	149^{i}	154^{h}	147^{i}	140^{j}	144^{C}
Z_1	153^{h}	176^{e}	162^{g}	167^{f}	162^{g}	165^{fg}	164^{B}
Z_2	186^{cd}	194^{b}	202^{a}	189^{c}	185^{d}	200^{a}	197^{A}
	155^{E}	173^{A}	171^{B}	170^{BC}	165^{D}	168^{C}	

Numbers followed by same letters in each column and rows, in each section, are not significantly ($P < 0.05$) different that the addition of ordinary zeolite (0, 5, 10 and 20 g kg^{-1}) in a soil with different levels of Cd (1, 5, 10 and 15 mg kg^{-1}) decreased the concentration of the WSEX fraction of Cd (72.0–88.0 to 30.0–66.4%) and concurrently the concentration of Cd in CARB and RES forms was increased. They reported that there was a significant negative correlation between soil pH and WSEX fraction of Cd as affected by application of zeolite levels. Generally, the addition of natural zeolite in contaminated soil can result in heavy metal stabilization in two ways: (1) the increase in soil pH reduces the competition of H$^+$ with heavy metals for adsorption by ligands (such as OH$^-$ and CO$_3$$^{2-}$) which leads to the formation of more stable heavy metal fractions, and (2) the application of zeolite increases cation exchange capacity (CEC) of soil and therefore enhances metal exchange in the zeolite structure (Peng et al. 2009). The application of only the zeolite at 3% (CZ$_1$) and 6% (CZ$_2$) increased the soil pH by 0.50 and 0.80 pH units, respectively (Table 7). A significant positive correlation ($R^2 = 0.61$ at $P < 0.05$) was found between soil pH and residual Cd fractions for all treatments. This confirms that the increase in of Cd RES forms in the zeolite treatments can be partially attributed to the increase in soil pH due to the application of zeolite. Application of the biochars without zeolite (Z_0 treatments) showed that the addition of CSB, LRB and SMB significantly reduced the WSEX fraction of Cd with respect to control treatment (C), while WSB and RHB treatments had no significant influence (Table 5). The CARB and FeMnOX fractions concentration of Cd was significantly decreased by the application of all of the biochars without zeolite, whereas OM fraction was significantly decreased by all biochars except SMB (Table 6). All of the biochar Z_0 treatments significantly increased the Cd concentration in the RES fraction by between 11.0 and 22.0% relative to the control (Table 6).

The mean comparison of the main effects of biochar application with/without zeolites showed that by application of CSB, LRB and SMB biochar treatments significantly decreased the Cd content in the WSEX form compared to control (Table 6). This can be attributed mainly to pH effects as strong negative correlation was found between the pH of treated soil and WSEX fraction of Cd ($R^2 = -0.73$, $P < 0.05$). The CSB, LRB and SMB biochars contained relatively higher amounts of CaCO$_3$ compared to the other biochars (Fig. 1) and increased soil pH to a greater extent than the other biochars (Table 7). Among the biochar treatments, only the LRB treatments significantly increased the CARB fraction of Cd, while the other biochars all significantly reduced the CARB relative to the control treatments without biochar (Table 6). The LRB treatments resulted in the highest soil pH among the biochar treatments with zeolite (Table 7) and were also shown to contain high amounts of CaCO$_3$ (Fig. 1). The addition of the other biochars with zeolite tended to lower soil pH relative to the zeolite only treatments (Table 7). This could explain why the CARB fraction was significantly increased in the LRB treatments, whereas it significantly decreased in the other biochar treatments (Table 6). The lowest concentration of CARB fraction was obtained in SMB treatment (219 mg kg^{-1}) among the applied biochar treatments (Table 5), which is unexpected since the FTIR spectra indicated that it contained the highest relative amount of CaCO$_3$ (Fig. 1). The maximum and the minimum Cd concentrations in CARB fraction were observed in CZ$_0$ (239 mg kg^{-1}) and SMBZ$_2$ (204 mg kg^{-1}) combined treatments, respectively (Table 6). Application of all biochar treatments significantly reduced the Cd concentration in FeMnOX fraction compared to control soil, so that the sequence of Cd concentration in this fraction were as C > SMB > LRB > RHB = WSB > CSB. The CZ$_0$ (103 mg kg^{-1}) combined treatment had the highest Cd concentration in FeMnOX fraction, and CSBZ$_2$ (68.5 mg kg^{-1}) combined treatment had the lowest Cd concentration in this fraction (Table 6). The OM fraction of Cd was significantly increased by SMB application, while the addition of other biochar treatments led to a significant reduction in the Cd concentration in OM form compared to control soil. The highest Cd concentration in OM fraction was in SMBZ$_0$ combined treatment, and the least concentration of OM fraction was in LRBZ$_2$ combined treatment (Table 6). The RES fraction was significantly increased compared to control soil by all of the biochar treatments so that the highest concentration of this form was obtained by CSB (173 mg kg^{-1}) application to soil. The CSBZ$_2$ and SMBZ$_2$ treatments had the highest Cd concentration in RES form, and CZ$_0$ combined treatment had the lowest concentration of RES fraction (Table 6). It could be attributed to the high P (Table 2) and lime content (Fig. 1) of these biochars (SMB and CSB), which would promote the formation of more stable Cd precipitates.

Table 7 Soil pH (1:5 soil/water ratio) values of the zeolite and biochar-treated Cd-contaminated treatments

Treatment	pH	Treatment	pH	Treatment	pH
CZ$_0$[a]	8.08^{k}	CZ$_1$	8.59^{d}	CZ$_2$	8.89^{b}
CSB + Z_0	8.34^{ghi}	CSB + Z_1	8.52^{de}	CSB + Z_2	8.72^{c}
WSB + Z_0	8.18^{j}	WSB + Z_1	8.28^{i}	WSB + Z_2	8.31^{hi}
RHB + Z_0	8.18^{j}	RHB + Z_1	8.41^{fg}	RHB + Z_2	8.72^{c}
LRB + Z_0	8.37^{gh}	LRB + Z_1	8.70^{e}	LRB + Z_2	8.97^{a}
SMB + Z_0	8.38^{gh}	SMB + Z_1	8.48^{ef}	SMB + Z_2	8.57^{d}

[a] Numbers followed by same letters are not significantly ($P < 0.05$) different

Given the above-mentioned results, the application of biochars caused the transformation of Cd in the soil from more bioavailable and mobile fractions to stabler forms. These changes were more obvious when biochar was applied with zeolite. Thus, the concomitant use of zeolite and biochar was more effective than separate application of them. Cui et al. (2013) examined the effect of the application of wheat straw biochar (prepared at 450 °C) at levels of 10, 20 and 40 t ha^{-1} in a Cd-polluted soil under wheat cultivation. They observed that the Cd concentration in CARB, FeMnOX and OM fractions was decreased and the concentration of RES fraction of Cd was increased significantly. Lucchinia et al. (2014) concluded that the repeated application of wood-derived biochar (*F. sylvatyca* L. prepared at 550 °C) (25 t ha^{-1}) in a contaminated soil increased the Cd concentration in RES fraction, but the CARB fraction was significantly reduced. Lu et al. (2016) investigated the effects of bamboo and rice straw biochars application with different mesh sizes (<0.25 and <1 mm) and at three rates (0, 1 and 5% w/w) on mobility and distribution of Cd using BCR sequential extraction method in a contaminated sandy loam soil. They reported that all biochar treatments significantly decreased the Cd concentration in acid extractable fraction. The concentration changes of OM fraction of Cd were variable and depended on the type, mesh size and rate of biochar application. The concentration of FeMnOX fraction of Cd was reduced by all the biochar treatments, but it was not significant. According to the results obtained by others and our results in this experiment, it seems that the type of applied biochar, rate of biochar application, mesh size of biochar, temperature and duration of biochar production and physicochemical properties of soil can be effective factors on transformation and distribution of Cd chemical forms as affected by addition of biochar in soil.

The relative index of heavy metals dynamic in soil was determined using mobility factor which obtained by sequential extraction procedure. The concentration of WSEX and CARB fractions has fundamental role as dynamic, bioavailable and high-risk forms of heavy metals for calculating the mobility factor in soil (Saffari et al. 2015). A high mobility factor value for heavy metals in soil is a sign of a high degree of availability (Kabala and Singh 2001). The mean comparison of main effects of zeolite treatments showed that with increasing the zeolite levels from Z_0 to Z_2, the mobility factor value of Cd was decreased by 10.0% compared to control. Also, application of all biochars (except LRB) resulted in the reduction in mobility factor values compared to control and the lowest value of it was found in SMB (47.7%) treatment. The interaction effects of treatments indicated that the $SMBZ_2$ combined treatment had the minimum value of mobility factor of Cd (44.0%) and thus, it was the best treatment in immobilization of Cd in soil. Generally, the possible mechanisms for the stabilization of heavy metals by biochars are: (a) the formation of precipitates such as phosphates (Jiang et al. 2012), (b) increases in the specific adsorption of metals (Jiang et al. 2012), (c) increases in electrostatic interactions and ionic exchange between metal cations and biochar derived protons (Uchimiya et al. 2010) and (d) increases in electrostatic interactions between metal cations and the activated functional groups caused by an increase in the soil pH (Park et al. 2011). The SMB contained the highest ash content (52.0%) among the biochars and also contained a relatively high P content (Table 2). This could promote the formation of precipitates with Cd as proposed by Jiang et al. (2012). The SMB biochar also contained the highest O + S content (12.9%) among the studied biochars (Table 2), which could lead to a greater abundance of oxygen- and sulfur-containing functional groups for specific adsorption (Jiang et al. 2012).

Pattern of Cd release affected by amendments

The Cd release patterns over 48 h were similar in all the soil treatments using EDTA extraction; however, the quantity and the rate of Cd desorption differed between treatments (Fig. 2). More than 50.0% of total released Cd during 48 h, desorbed during the first 2 h. Therefore, desorption of Cd in control and treated soils was initially fast and continued with a slower rate until equilibrium was reached (Fig. 2). Similar to our results, Saffari et al. (2015) and Zahedifar et al. (2012) reported the two-step process of Cd and Zn desorption from calcareous soils, respectively. Mustafa et al. (2004) reported that the Cd desorption was relatively rapid during the initial steps of desorption extractions and thereafter became progressively slower with each desorption step. Rapid and subsequent slow releases of heavy metal may be attributed to the existence of sites with different bond energy. Initial rapid release of heavy metals from soil shows the desorption of these metals from the water-soluble form and also from the adsorption sites of lower bonding energy (exchangeable fraction), and in following, slow release of metals indicates the release of metals from the sites of relatively higher bonding energy than the exchangeable form and other chemical pools in dynamic equilibrium with the exchangeable form (Kandpal et al. 2005). Use of all treatments led to a significant decrease in desorption of Cd extracted by EDTA during 48 h compared to the control soil. The lowest release of Cd was observed in $SMBZ_2$ (171 mg kg^{-1}) combined treatment, and this reduction was about 54.2% in comparison with the control soil. This observation is in agreement with the mobility factor results obtained with the Cd chemical fractionation. Zhang et al. (2013) also reported that quantity of EDTA-extractable Cd was reduced after addition of oil mallee biochar and wheat chaff biochar in a Cd-contaminated soil. Biochar can effectively reduce the availability of heavy metals by adsorption, ion exchange, surface complexation and precipitation due to its highly porous micro-structure, active functional groups, high pH, surface area and CEC (Bian et al. 2014). Also, the reduction in the EDTA-extractable Cd in soil by addition of zeolite can be related to its high CEC (80.1 $\text{cmol}_c\ \text{kg}^{-1}$) and pH (10.0).

Fitting of Cd desorption data to kinetic models

Kinetic equations including zero order, first order, second order, third order, the parabolic diffusion, two-constant rate and simple Elovich (Table 5) were used for describing the release kinetics of Cd up to 48 h. The amounts of Cd desorbed by EDTA were poorly fitted by zero-order, first-order, second-order and third-order kinetic equations in all treatments. In order kinetic equations, with increasing the reaction order of equations from zero to third, the coefficient of determination (r^2) decreased in treated and control soils which was also reported by others (Saffari et al. 2015; Rezaei Rashti et al. 2014). It was obvious that patterns of Cd release could not be described by a simple rate equations because desorption of soil Cd is controlled by several factors including Fe oxides content (Davis and Kent 1990), type and contents of clay minerals (Jobstmann and Singh 2001), organic matter and the other solution conditions such as pH, temperature, aging and Cd concentration (Mustafa et al. 2004). Even though the parabolic diffusion and simple Elovich equations had the relatively high values of r^2 (0.84 and 0.95, respectively), but their standard error of estimate (SEE) values (26.1 and 15.4, respectively) were considerably more than the two-constant rate equation ($r^2 = 0.93$ and SEE $= 0.11$). Therefore, based on the high values of r^2 and low values of SEE obtained from used models, two-constant rate equation was selected as the best model for describing the release kinetics of soil Cd. The study of Rezaei Rashti et al. (2014) on the kinetics of Cd desorption from soils of Northern Iran indicated that parabolic diffusion, two-constant rate, and Elovich kinetic models were suitable for describing the trend of Cd desorption.

Effect of amendments on Cd desorption using constants of two-constant rate model

As Cd desorption from the soil was adequately described by a two-constant rate model, the effects of amendments on Cd desorption kinetic were studied by the use of constants obtained from it. The two-constant rates equation is as follows: $q_t = at^b$ or $\ln q_t = \ln a + b \ln t$, where q_t is the quantity of the Cd desorbed in time t, "a" is the amount of initial Cd desorption $(\text{mg Cd kg}^{-1}\ \text{h}^{-1})^b$, and "$b$" is desorption rate coefficient of the line slope of equation $(\text{mg Cd kg}^{-1})^{-1}$. The main effects of biochars and zeolite levels and their interactions on "a" and "b" constants were statistically significant at $P \leq 0.01$ (Table 8). Constant "a" decreased significantly with increasing the zeolite levels (Table 8). All of the biochar treatments significantly decreased constant "a" compared to the control, except WSB treatment which caused a significant increase of it (Table 8). The greatest reduction in constant "a" due to biochar application was observed in LRB treatment (38.0% on average relative to the control). At Z_0 and Z_1 zeolite levels, the lowest value of constant "a" was in the LRB treatment, while at Z_2 zeolite level, the lowest value was in the CSB treatment (Table 8). Generally, the application of zeolite and biochars (except WSB) decreased the magnitude of released Cd in the soil.

Coefficient "b" was also significantly reduced with increasing levels of zeolite (Table 8). All of the biochar treatments significantly decreased coefficient "b" compared to the control, except LRB treatment which caused a significant increase (Table 8). The greatest relative decrease in the constant "b" was obtained in WSB treatment (Table 8). Thus, in the LRB biochar treatments, a reduction in constant "a" went together with in an increase in coefficient "b," and the opposite trend was true for the WSB treatments (Table 8). The interactive effects showed that coefficient "b" was reduced by increasing the zeolite levels, in WSB, RHB and SMB treatments while in C, CSB and LRB treatments, it was increased (Table 8). It was found that the effect of zeolite application on changes in

Table 8 Coefficients of two-constant rate model as affected by biochar and zeolite levels application in a Cd-polluted calcareous soil

Treatment	C	CSB	WSB	RHB	LRB	SMB	
a $(\text{mg Cd kg}^{-1}\ \text{h}^{-1})^b$							
Z_0	190^b	130^h	215^a	122^k	98.8^n	126^i	147^A
Z_1	153^f	123^j	153^g	158^d	95.9^o	101^m	131^B
Z_2	115^l	86.6^r	167^c	155^e	89.0^q	95.8^p	118^C
	153^B	112^D	178^A	145^C	94.6^F	108^E	
b $(\text{mg Cd kg}^{-1})^{-1}$							
Z_0	0.18^j	0.18^i	0.13^n	0.26^d	0.28^c	0.21^f	0.208^A
Z_1	0.21^g	0.19^h	0.12^o	0.18^l	0.29^b	0.18^k	0.203^B
Z_2	0.25^e	0.21^f	0.11^p	0.16^m	0.31^a	0.17^l	0.193^C
	0.21^B	0.19^D	0.12^F	0.20^C	0.29^A	0.18^E	
ab							
Z_0	35.0^a	24.1^l	27.6^h	31.9^b	27.9^e	26.5^j	28.8^A
Z_1	31.6^c	23.2^m	19.1^n	27.8^f	27.5^i	18.1^p	24.5^B
Z_2	29.0^d	17.6^q	18.2^o	24.9^k	27.7^g	16.9^r	22.4^C
	31.8^A	21.7^D	21.6^E	28.2^B	27.7^C	20.5^F	

Numbers followed by same letters in each column and rows, in each section, are not significantly ($P < 0.05$) different the "*b*" coefficient value was dependent on the type of applied biochar in soil. Generally, the application of zeolite levels and biochars (except LRB) caused a decrease in the Cd release rate from soil.

Dang et al. (1994) noted that if constant "*b*" $\leq$0.25 in the two-constant rate model, then more than one diffusion site are involved in Zn desorption from soil. In the present study, constant "*b*" was lower than 0.25 in most applied treatments; thus, the role of different diffusion sites in controlling the Cd desorption is confirmed once again. Similar involvement of sites with different bond energy and reactivity in Cd release from soils had been also reported by Krishnamurti et al. (1999) In the two-constant rate equation, q_t can be differentiated with respect to *t*, resulting in $d_q/d_t = abt^{b-1}$ and when $t = 1$, the previous equation can be written as $d_q/d_t = ab$, and "*ab*" may be taken as the initial desorption rate of a soil element (Dalal 1985). The main effects of biochars and zeolite levels and their interactions on the value of "*ab*" constant were statistically significant at $P \leq 0.01$. With increasing zeolite levels from Z_0 to Z_2, the "*ab*" constant was significantly reduced by 22.4% (Table 8). Furthermore, application of all biochar treatments caused a significant reduction in the value of "*ab*" constant. The sequence of the "*ab*" constant in the biochar treatments was as follows: C > RHB > LRB > CSB > WSB > SMB (Table 8). The interaction effects indicated that the lowest "*ab*" constant was obtained in the SMBZ$_2$ combined treatment, whereas the highest value was found in the CZ$_0$ combined treatment (Table 8). Thus, the addition of zeolite and biochars to the soil decreased the initial Cd desorption rate considerably. The "*a*" and "*b*" constants in the two-constant rate equation showed no significant correlation with mobility factor of Cd, whereas there was a positive and significant correlation between "*ab*" constant and mobility factor of Cd ($r = 0.61$, $P \leq 0.01$). Initial desorption of Cd is associated with fractions that have lower bonding energy such as WSEX and CARB forms (Kandpal et al. 2005), which are determinative in calculating the mobility factor of Cd; this significant correlation with the "*ab*" constant was expected. According to the calculated Cd mobility factor, the best treatment for stabilization of Cd in soil was the SMBZ$_2$ combined treatment; likewise, the "*ab*" constant also confirmed it (Table 8). Therefore, it seems that "*ab*" constant derived from two-constant rate equation can be used as an indicator of Cd mobility and bioavailability in soil.

Conclusion

In general, the results showed that natural zeolite immobilized Cd in soil by enhancing the concentration of RES fraction and decreasing the other more available fractions. This was mainly attributed to the increase in soil pH and resulting increase in Cd sorption due the application of the zeolite. Transformation in the chemical fractions of Cd and their conversion into less bioavailable forms were also observed with application of all biochars with or without zeolite, but these changes in chemical forms varied from one biochar to another. Among the biochars, SMB was the most effective at enhancing Cd immobilization, most likely due to its relatively high ash, CaCO$_3$ and P content, and its high O + S content. The application of zeolite and biochars (except LRB) caused a significant decrease in mobility factor of Cd compared to the control treatment. The interaction effects of treatments indicated that the SMBZ$_2$ combined treatment had the lowest mobility factor of Cd. Desorption of Cd in control and treated soils was initially fast and followed with a slower rate until equilibrium was reached. Initial rapid and subsequent slow releases of heavy metal may be attributed to the existence of places with different energy. Use of all treatments led to a significant decrease in desorption of Cd extracted by EDTA during 48 h compared to the control soil. The lowest release of Cd was observed in SMBZ$_2$ combined treatment, which was 54.2% lower than the control soil. Based on the high values of R^2 and low values of SEE, the two-constant rate equation was selected as the best model for describing the release kinetic of soil Cd. A positive and significant correlation was found between "*ab*" constant in the two-constant rate equation and mobility factor of Cd ($r = 0.61$, $P \leq 0.01$). The lowest value of "*ab*" constant was obtained in SMBZ$_2$ combined treatment. Generally, the present study showed that from the practical point of view, all treatments were effective in Cd stabilization; however, combined application of 3% SMB with 6% natural zeolite (SMBZ$_2$) was the most effective treatment to reduce availability and promote stabilization of Cd in the contaminated calcareous soil. Further research is needed to evaluate the relationship between Cd chemical forms as influenced by selected treatments and plant uptake in calcareous contaminated soils.

Acknowledgements This work was supported by college of agriculture and natural resources of Darab, Shiraz University, Iran.

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