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ORIGINAL PAPER

Impact of Biochar on Release Kinetics of Pb (II) and Zn (II) in a Calcareous Soil Polluted with Mining Activities

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Abstract

Release kinetics governs the detachment and migration of potentially toxic trace elements (PTEs) over time between the solid phase and soil solutions. The assessment of PTEs' release behavior through time supports more accurate prediction models of toxicity in highly polluted soils. Recently, biochar, a charcoal black carbon ameliorant, was extensively applied for decreasing the release of Zn and Pb to the soil solution. This study was arranged during a short-term (45 days) incubation experiment to estimate the possible effects of walnut leaves (WL) and their biochars produced at three temperatures (200 (B200), 400 (B400), and 600 (B600) °C) on the kinetics of Zn and Pb release in a naturally calcareous and highly polluted soil. Results showed that the biochars could reduce the release of Zn and Pb to the soil solution. The rate of Zn release ("*b*" in power function) at different biochar levels was 0.35 (2% B600)–0.38 (control) (mg $kg^{-1})^{-1}$, respectively; also, the release of Pb was 0.23 (2% B600)–0.33 (control) (mg $kg^{-1})^{-1}$, respectively. The results illustrated that a lower concentration of these metals was associated with exchangeable and oxides of Fe-Mn, whereas the higher content of residual fractions of Zn and Pb reduced the release of Zn and Pb in soils treated with biochar. Overall, the more the level and temperature of biochar increased, stabilizing PTEs through changing the distribution of metals in the soil, the more biochars succeeded significantly in lessening the release of PTEs, which ultimately could retard the further toxicity in the soil solution.

Keywords Pyrolysis temperature · DTPA · Fractions · Modeling release kinetics · Desorption

1 Introduction

Soil has drastically become a major reservoir of potentially toxic trace elements (PTEs) due to indiscriminate man-made endeavors, especially when extracting valuable minerals or geological materials from the ground in mining areas (Kabiri et al., 2019; Lahori et al., 2020; Feng et al., 2020). Potentially toxic trace elements can reach the food supply, contaminate microbiota and macrobiota, and ultimately increase hazards to human beings (Lahori et al., 2019). The detrimental effects of PTE exposure and its poisoning of the soil depend on their distribution between various soil ingredients since their total contents cannot completely predict their migration and noxious effects in the soil (Moore et al., 2015). They can bond to soil components and form several partitions due to the physicochemical properties of soil, including precipitates such as iron and manganese oxides; exist as carbonates; adhere to organic matter; become trapped in residuals; and attach to silicates (Chibuike and Obiora, 2014). Metals that are made into soluble and exchangeable forms or associated with carbonate fractions are most toxic, while others have a lower exposure and are considered less hazardous pollutants (Jalali et al., 2019). Additionally, contamination severity depends heavily on the intensity and retention capacity factors of soil (Moral et al., 2005). In fact, the partition of PTEs entering the soil solution is more important than their content in the solid phase (Degryse et al., 2009). Because this part determines trace elements transport fate, movement, and toxicity (Kouassi et al., 2019), the bioavailable and mobile fractions of metals are soluble content in the soil solution, as well as the content that is retained by the solid phase, provided that it can be transferred into the liquid phase of the soil (Moore et al., 2015).

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Metal bioavailability and fractionation in the soil are measured through release kinetics and sequential extraction methods (Kouassi et al., 2019). In non-polluted soils, the distribution of metals among different components is based on their physicochemical properties and soil aspects, but in highly polluted soils, PTEs' partitions are affected by the metal content and time intervals (McLaren and Ritchie, 1993; Han and Banin, 2000). In other words, the severity of toxicity depends strongly on the release rate of PTEs associated with soil components from the solid phase into the soil solution versus time (Moore et al., 2015). Metals bound to exchangeable and carbonate fractions tend to be more mobile and detach faster from the soil solution initially, while metals associated with Fe-Mn oxides, organic matter, and residuals settle more tightly for a while and are expected to be removed from soil components for a long duration. Therefore, more time is needed for their release (Kotoky et al., 2003; Motaghian and Hosseinpur, 2013). Thus, believing that both sequential and kinetic extraction techniques are more feasible and pragmatic than arranging a single approach, there is a growing interest in applying both procedures among researchers (Gismera et al., 2004). Sequential extraction procedures determine metal contents in different soil particles, and kinetic extraction approaches measure the elements' content and dissociation speed of weak and strong bonds between metals and soil constituents (Fangueiro et al., 2005). They can be utilized together in developing countries with insufficient research institutions. Both of these procedures help to discover the geochemical fractionations and migrations of PTEs in soils during specific times (Kouassi et al., 2019).

Biochar, as a nontoxic sorbent with highly proliferous fragments, is supposed to be a promising ingredient for alleviating PTEs from soils. As is prepared inside a sealed container with no or very low air pressure, biochar finds its extraordinarily high organic carbon in a polarity aromatic structure and high oxygen-containing acid group content in order to grasp PTEs with higher sorption efficiency than other organic matters (Wang et al., 2015; Abdallah et al., 2019). Studying Zn and Pb fractionation and phytotoxicity in naturally calcareous and highly polluted soil, Kabiri et al. (2019) concluded that biochar reduced Zn and Pb content in plant tissues and promoted gradual maize growth responses through modifying metals' fractions. They stated that biochars fractioned Zn and Pb from readily available partitions (soluble, exchangeable, associated with carbonates, associated with Fe-Mn oxides) to less accessible forms (associated with organic matter and residual). Therefore, the metals' phytotoxicity levels were reduced.

The absorption of Zn and Pb by plants from a soil solution is a continuous process and is strongly influenced by the release of metal from solid fractions to soil solutions. Therefore, the release rate of metals is an important characteristic of polluted soils. Also, the effects of biochars produced at various temperatures are important for the release kinetics of Zn and Pb from highly polluted calcareous soils. However, detailed information about the mechanism of biochars produced at various temperatures, in addition to the metals' release kinetics in highly polluted and calcareous soils treated with biochars, is still limited. Thus, in this study, the use of walnut leaves' biochars is investigated to assess the kinetics of Zn (II) and Pb (II) release. We intend to discern if pyrolysis temperature and application level have significant effects on release kinetics in all treatments. Therefore, this research aims to (i) evaluate the effects of walnut leaves' biochars on Zn and Pb release characteristics from the biochar-treated soils, (ii) evaluate the relationship between the release characteristics of Zn and Pb and their sequential extraction components from the soils treated with biochars, and (iii) evaluate the ability of different mathematical models in order to choose the best model for describing Zn and Pb release. The hypotheses tested are as follows: (i) different biochars cannot change the cumulative release concentrations of Zn and Pb in a highly polluted soil and (ii) a change in metal fractions cannot modify the Zn and Pb release characteristics in highly polluted soil.

2 Materials and Methods

2.1 Soil Sampling

This study was conducted in a historical mining (Bama mine) area in the city of Sepahanshahr, Isfahan Province, Central Iran. The area was located at a latitude of 33° 30′ 79″, 32° 33′ 47″ N and a longitude of 51° 40′ 38″, 51° 35′ 24″ E. The study area is affected by mining activities exploiting raw materials containing Zn and Pb. Bama mines have been active during the last 70 years. They contain some sites that are mostly exploited as open mines. The exploitation of active mines has released large quantities of Zn and Pb into the surrounding surface soils in a vast area. The soil was collected from the surface layer area that is adjacent to the mine. After preparing samples similar to our previous research, some major properties were evaluated. The soil was classified as Calcigipsids (Staff SS, 2014). It was non-saline (EC = 0.82 dS m^{-1}) and slightly alkaline (pH = 7.5), and had a 28.4% calcium carbonate equivalent. The texture was loamy sand (sand = 78%, silt = 15%, and clay = 7%) with low organic matter content (OC = 0.13%) and a cation exchange capacity (CEC = 10.7 $cmol_+$ kg^{-1}). The pseudo-total Zn and available Zn were 35.758 and 228.8 mg kg^{-1}, respectively, while the pseudo-total Pb and available Pb were 7933 and 432.8 mg kg^{-1}, respectively. The contents of total nitrogen, available P, and K were 0.015%, 13.07, and 43 mg kg^{-1}, respectively (Kabiri et al., 2019).

2.2 Biochar Production and Characterization

Biochars were produced from walnut leaves (*Juglans regia* L.). We described the production procedure details and physiochemical properties of the walnut leaves (B0) and biochars produced at 200, 400, and 600 °C (B200, B400, and B600) in our previous study. In particular, B0 and B200 were acidic in reaction (pH = 4.8 and pH = 5.2), but B400 and B600 were alkaline in nature (pH = 9.3 and pH = 10.4). B600 exhibited the greatest EC value (8.06 dS m^{-1}). Others correspondingly ranked in the following order: B400 (5.63 dS m^{-1}) > B200 (4.42 dS m^{-1}) > B0 (3.11 dS m^{-1}). Although all biochars had a relatively low surface area (less than 10 m^2 g^{-1}), with regard to higher temperatures, their surface area was found in ascending order. The CEC of the walnut leaves exceeded that of biochars (30.5 $cmol_+$ kg^{-1}). It was in descending order for a greater temperature of biochars (B200 (28.5 $cmol_+$ kg^{-1}) > B400 (22.9 $cmol_+$ kg^{-1}) > B600 (19.9 $cmol_+$ kg^{-1})) (Kabiri et al., 2019); thus, our previous experience documented that higher pyrolysis temperatures increased pH, ash content, BET, and aromaticity, which were the most important characteristics affecting adsorption and release of PTEs in soil according to previous results (Dokht et al., 2017).

2.3 Incubation Experiments

Three kilograms of air-dried polluted loamy sand soil was incorporated in plastic pots. Walnut leaves and biochars were passed through a 1-mm sieve and were homogenously mixed into pots at levels of 0.5%, 1%, and 2% total dry soil weight of 13 treatments with three replicates. Then, the soils were irrigated up to 70% of field capacity (FC). Perforated plastic lids covered the pots to reduce water loss and allow gas exchange. The pots were placed in optimized greenhouse conditions and incubated for 45 days at 25 °C. At the end of incubation, 200 g of soil samples was removed from the pots. Then, the samples were analyzed for the release kinetics and fractionation experiments.

2.4 Zn and Pb Release Kinetics

Successive extractions were considered when studying the kinetics of Zn and Pb release from the treatments. Two-gram subsamples of each incubated soil sample (39 tubes) were suspended in 20 ml of diethylenetriaminepentaacetic acid (DTPA) equilibrated at 25 ± 1 °C for 2, 4, 8, 24, 48, 72, 96, 120, 144, 168, 336, and 504 h by shaking for 15 min before and after incubation. The Zn and Pb contents were measured utilizing an atomic absorption spectrophotometer instrument (model G.B.C 932). The Zn and Pb release was evaluated during specified times and considering different equations (Motaghian and Hosseinpur, 2013). Three models were fitted by the least-square regression analysis to determine the best equation showing the release from the soils (Table 1).

The standard error of the estimate (SEE) was calculated by Eq. (1):

$$\mathrm{SEE} = \left[\frac{\sum\left(M - M^*\right)^2}{(n-2)}\right]^{0.5} \quad (1)$$

where M and M^* represent the calculated contents of Zn and Pb in soil at time t, respectively, and n is the number of data points evaluated.

2.5 Zn and Pb Fractionations

The five-stage procedure (Tessier et al., 1979) was adopted for fractionation of zinc and lead in soil including the following: (1) 1 M magnesium chloride for exchangeable Zn and Pb; (2) 1 M sodium acetate for Zn and Pb associated with carbonates; (3) 0.04 M hydroxylamine–hydrochloride in 25% acetic acid for Zn and Pb associated with Fe-Mn oxides; (4) 30% hydrogen peroxide and 0.02 M nitric acid for Zn and Pb associated with organic matter; and ultimately (5) residual fractions were calculated by determining the difference between pseudo-total amount of Zn and Pb (Sposito et al., 1982) and the sum of their fractions. The concentration of Zn and Pb fractions was determined by applying an atomic absorption spectrophotometer instrument (model G.B.C 932).

2.6 Statistical Analyses

The two-way ANOVA was adopted to analyze the effect of amendments on cumulative release amounts of Zn and Pb through 2 to 504 h and their fractions. Treatment means were separated at the 5% significance level using Fisher's LSD tests. The Pearson correlation was performed between the cumulative release amounts of Zn and Pb and the parameters of kinetic models with fractions of Zn and Pb. Statistical analyses of data were assessed by Statistica 8.

Table 1 Kinetic models used in this study

Kinetic equation	Expression form	Reference
Parabolic diffusion	$M_t = a + R\,t^{0.5}$	Havlin et al. 1985
Power function	$M_t = a\,t^b$	Havlin et al. 1985
Simplified Elovich	$M_t = a_e + 1/\beta\ \ln t$	Havlin et al. 1985

M_t is the amount of the metals (mg kg^{-1}) release at time t (h) and a, a_e, R, b, and $1/\beta$ are constants

3 Results

3.1 Zn and Pb Release Kinetics

The concentrations of Zn (35,758 mg kg^{-1}) and Pb (7933 mg kg^{-1}) were very high in the studied soil, following the different mining operations developed in the active mines. The authors reported heavily contaminated sites around the world in previous works (Cheng et al., 2015; Lu et al., 2018).

Different equations (Table 1) were fitted to illustrate the kinetic behavior of Zn and Pb in treatments by a DTPA solution from 2 to 504 h. The equations were evaluated by calculating the highest coefficient of determination (r^2) and the lowest value of the standard error of estimate (SEE) among equations for both metals (Havlin et al., 1985). According to the highest r^2 (0.99 and 0.99 for Pb and Zn, respectively) and lowest SEE (51 and 69 for Pb and Zn, respectively), the best reaction rate can be expressed by the power function equation (Table 2). Also, parabolic diffusion and simplified Elovich models were used to sufficiently describe Pb and Zn release kinetics owing to $r^2 = 0.96$ and 0.96 and SEE = 111 and 99 mg kg^{-1}, respectively, for Pb, and $r^2 = 0.98$ and 0.94 and also SEE = 109 and 139 mg kg^{-1} for Zn, respectively (Table 2). These mathematical equations have been useful in explaining the cumulative release and release rate of Pb and Zn and, also, other elements in previous studies (Taghdis et al., 2016; Zahedifar and Moosavi, 2017; Boostani et al., 2019; Motaghian et al., 2020).

The results showed that the effect of pyrolysis temperatures and application levels of biochars was significant ($p < 0.01$) on cumulative amounts of Zn and Pb extracted by DTPA. In order of priority, pyrolysis temperature was the most important factor in affecting changes in the cumulative amounts of Zn and Pb (Table S1, Appendix). The difference in cumulative amounts of Zn between soils treated with biochars produced at all temperatures was significant ($p < 0.05$). The cumulative amounts of Zn diminished significantly ($p < 0.05$) by 4–20%, with an increase in the pyrolysis temperature of biochars. For Pb, the difference between treatments was significant ($p < 0.05$), but not for soils treated with B200 and walnut leaves. Soils treated with B400 and B600 decreased in cumulative amounts of Pb by 33% and 48%, respectively, compared with walnut leaves (Table S2, Appendix).

The cumulative amount of Zn differed within all treatment levels ($p < 0.05$), whereas additions of 0.5% and 1% of biochar to the soil had no influence for cumulative amounts of Pb. Treating the soil with 1% and 2% of biochar declined the cumulative amounts of Zn by 5% and 10%, and, also, the cumulative amounts of Pb by 4% and 13%, respectively, compared with walnut leaves ($p < 0.05$) (Table S2, Appendix).

In fact, all biochars demonstrated significant decreases in Zn and Pb cumulative amounts ($p < 0.05$) compared with the control group. The application of 2% of B200, B400, and B600 reduced the cumulative amounts of Zn by 12%, 21%, and 28%, whereas the cumulative amounts of Pb were reduced by 25%, 53%, and 62%, respectively, in comparison with the control group (Table S2, Appendix) (Fig. 1).

An identified indicator of Zn and Pb release rates in the soil is assessed by considering defined parameters in the power function, parabolic diffusion, and simplified Elovich equations. Table 3 presents the equations rates' constants. The ranges of "b" and "$a \times b$" values were 0.35 (2% B600)–0.38 (control) (mg $kg^{-1})^{-1}$ and 76 (2% B600)–99 (0.5% walnut leaves), respectively, for Zn, whereas they were 0.23 (2% B600)–0.33 (control) (mg $kg^{-1})^{-1}$ and 111 (2% B600)–224 (control) for Pb, respectively. As mentioned above, "b" values were less than 1, illustrating that Zn and Pb detachment declined with time (Taghdis et al., 2016). Parameters "a" and "b" were derived from the power function equation, which illustrated the Zn and Pb release rates of the soil (Olama et al., 2010). Moreover, the beginning release rate of these metals was evaluated considering parameter "$a \times b$" (Allen et al., 1995). According to Reyhanitabar and Gilkes (2010), "a" is the number of accessible surface sites for releasing metals and "b" is the tendency of metals to these sites. Therefore, the number of accessible surface sites for release and tendency to surface sites was bigger for Pb than for Zn. It seemed that Pb resided on reachable sorption sites with less binding energy. Therefore, Pb is released more rapidly than Zn from the soil components. Based on priority order, the maximum value of "b" (obtained from the power function) for Pb was observed in the control group as 0.33 (mg $kg^{-1})^{-1}$, whereas it decreased approximately by 0.30 in soils treated with walnut leaves, B200, and B400. Therefore, the rate of release of metals, as measured by the "b" value, decreased with increasing the pyrolyzing temperature of biochar synthesis. So, in the presence of B600, it declined by 0.20 (mg $kg^{-1})^{-1}$. This factor for Zn was 0.38 (mg $kg^{-1})^{-1}$ in the

Table 2 Coefficient of determination (r^2) and standard error of the estimate (SEE) of various kinetic models for Zn and Pb release in treatments ($n = 3$)

Equation	R^2		SEE (mg kg^{-1})	
	Range	Mean	Range	Mean
Zn				
Parabolic diffusion	0.96–0.97	0.97	109–134	120
Simplified Elovich	0.91–0.94	0.93	139–230	185
Power function	0.98–0.99	0.99	69–92	79
Pb				
Parabolic diffusion	0.94–0.96	0.95	111–317	200
Simplified Elovich	0.92–0.96	0.94	99–417	224
Power function	0.98–0.99	0.98	51–226	118

All coefficients of determination (r^2) are significant at the 0.01 level

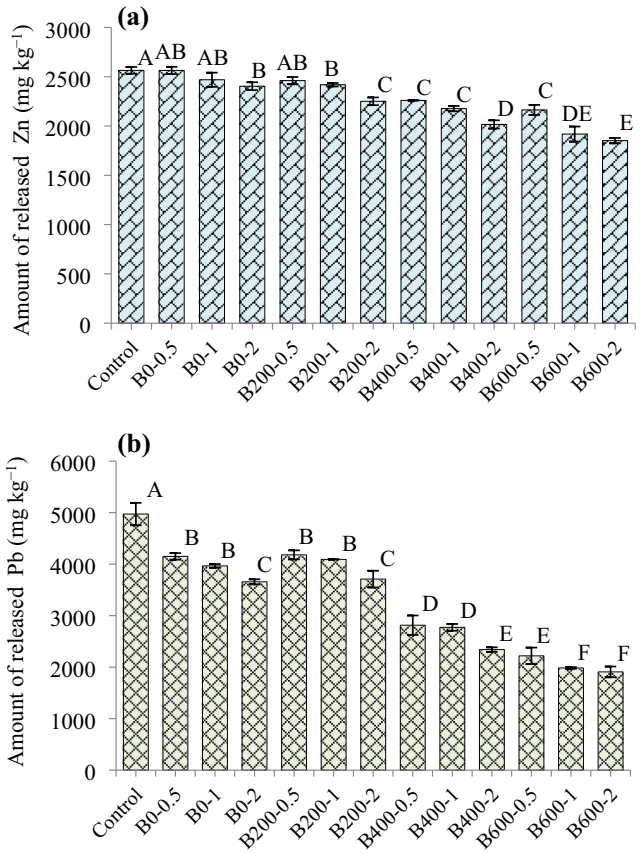

Fig. 1 Cumulative amount of Zn and Pb release (mg kg^{-1}) in all soils. Means values with different letter(s) represent significant differences between treatments by Fisher LSD's test at $p < 0.05$. Values are mean ± standard errors ($n = 3$). Control, untreated soil; B0-0.5, 0.5% walnut leaves; B0-1, 1% walnut leaves; B0-2, 2% walnut leaves; B200-0.5, 0.5% biochar produced at 200 °C; B200-1, 1% biochar produced at 200 °C; B200-2, 2% biochar produced at 200 °C; B400-0.5, 0.5% biochar produced at 400 °C; B400-1, 1% biochar produced at 400 °C; B400-2, 2% biochar produced at 400 °C; B600-0.5, 0.5% biochar produced at 600 °C; B600-1, 1% biochar produced at 600 °C; B600-2, 2% biochar produced at 600 °C

control group, but it declined by 0.35 $(mg\ kg^{-1})^{-1}$ in the soils treated with B600. Also, the "$a \times b$" value was lower in the control group than in soils treated with walnut leaves, but it was higher when compared with soils treated with biochars.

In the present study, values of "a_e" for Zn and Pb (derived from the Elovich equation) changed from − 364 to − 198 and − 160 to 134 mg kg^{-1}, respectively, after incorporating walnut leaves and biochars into the soil. Meanwhile, "1/β" decreased from 400 to 295 mg kg^{-1} h^{-1} and from 757 to 253 mg kg^{-1} h^{-1}, respectively, for Zn and Pb.

In the present experiment, the release rate constant "R" of the parabolic equation for Zn and Pb extracted by DTPA-TEA varied from 111 to 80 and 208 to 68 mg kg^{-1} h^{-1}, respectively (Table 3).

The amount and rate of the metals extracted by DTPA solution could be attributed to the metal distribution in solid phases of the soil (metals' fractions) (Brunori et al., 2005; Farshadirad et al., 2017). Therefore, the fractions of Zn and Pb in the soil treated with biochars may be explained by the amount and rate of the metals extracted by DTPA change after the addition of biochars produced at pyrolysis temperature.

3.2 Fractions of Zn and Pb

Pyrolysis temperature and the level of application had a significant effect ($p < 0.01$) on Pb fractions. The interaction between pyrolysis temperature and application level was significant only on exchangeable Pb and Pb associated with Fe-Mn oxides ($p < 0.01$), whereas pyrolysis temperature showed a significant ($p < 0.01$) impact on exchangeable Zn, Zn associated with Fe-Mn oxides, and residual Zn. The level of application influenced Zn associated with Fe-Mn oxides ($p < 0.05$), exchangeable Zn, and Zn associated with organic matter ($p < 0.01$). The impacts of temperature and level of application were effective on exchangeable Zn and residual Zn ($p < 0.01$) (Table S1, Appendix).

The interaction between pyrolysis temperature and the application level of biochar was effective on exchangeable Zn and Pb, which demonstrated that the effect of biochar application level depended on pyrolysis temperature. Treating the soil with 2% B600 decreased exchangeable Pb by 20% and 40% when compared with that with B200 and walnut leaves, respectively (Fig. 3(a)). It also declined exchangeable Zn by 20% and 33% compared with that with B400 and walnut leaves, respectively (Fig. 2(a)).

Compared with the control, treatments with various application levels and pyrolysis temperatures of biochar proved effective to decrease Pb associated with carbonates (with the exception of soils treated with 0.5% and 1% walnut leaves) (Fig. 3(b)). Also, soils treated with 0.5% walnut leaves, 0.5% and 1% B200, 0.5% B400, and different application levels of B600 decreased Zn associated with carbonates ($p < 0.05$) (Fig. 2(b)).

The application of 2% B600 in the soil reduced the Pb associated with Fe-Mn oxides by 15%, 27%, and 34% compared with that of 2% B400, B200, and walnut leaves, respectively. Additionally, the Pb associated with Fe-Mn oxides was reduced in soils that were treated with biochar produced at all pyrolysis temperatures (Fig. 3(c)). However, with regard to Zn, the addition of 0.5% and 1% walnut leaves, 2% B200, 2% B400, and different application levels of B600 reduced the Zn associated with Fe-Mn oxides ($p < 0.05$) (Fig. 2(c)).

Furthermore, the Pb associated with organic matter was enhanced after the application of different levels of biochars produced at B400 and B600°C compared with walnut leaves (Fig. 3(d)). Zinc associated with organic matter increased by applying 1% and 2% walnut leaves, 1% and 2% B200, 2% B400, and 2% B600 (Fig. 2(d)). In comparison with the control, residual Pb increased in the soils treated with various levels of biochars (Fig. 3(e)), whereas soils treated with

Table 3 Parameters of models used to describe release kinetics of Zn and Pb in treatments ($n = 3$)

Treatments	Parabolic diffusion		Simplified Elovich		Power function		
	a mg kg^{-1}	R mg kg^{-1} h$^{-1/2}$	a_e mg kg^{-1}	1/β mg kg^{-1} h^{-1}	a mg kg^{-1} h^{-1}	b (mg kg^{-1})$^{-1}$	$a \times b$
Zn							
Control	250 ± 5	112 ± 5	− 264 ± 3	400 ± 5	243 ± 4	0.38 ± 0.01	93 ± 2
B0-0.5	295 ± 12	111 ± 13	− 223 ± 11	399 ± 3	270 ± 7	0.37 ± 0.01	99 ± 1
B0-1	289 ± 8	106 ± 5	− 209 ± 9	383 ± 5	263 ± 8	0.37 ± 0.04	96 ± 3
B0-2	293 ± 10	104 ± 7	− 198 ± 4	375 ± 6	264 ± 5	0.37 ± 0.03	95 ± 3
B200-0.5	303 ± 12	105 ± 4	− 196 ± 13	381 ± 4	271 ± 11	0.37 ± 0.03	98 ± 2
B200-1	277 ± 10	104 ± 6	− 214 ± 5	377 ± 12	255 ± 12	0.37 ± 0.01	94 ± 4
B200-2	272 ± 7	96 ± 7	− 183 ± 6	348 ± 11	245 ± 8	0.36 ± 0.04	89 ± 3
B400-0.5	277 ± 13	98 ± 2	− 201 ± 3	358 ± 2	254 ± 6	0.36 ± 0.01	91 ± 2
B400-1	265 ± 4	94 ± 4	− 189 ± 7	342 ± 13	241 ± 10	0.36 ± 0.05	87 ± 3
B400-2	228 ± 12	88 ± 5	− 192 ± 5	320 ± 6	214 ± 4	0.37 ± 0.02	79 ± 1
B600-0.5	288 ± 7	94 ± 3	− 178 ± 12	345 ± 9	258 ± 9	0.35 ± 0.01	90 ± 4
B600–1	249 ± 6	83 ± 5	− 158 ± 3	304 ± 4	223 ± 3	0.35 ± 0.02	78 ± 5
B600-2	240 ± 11	80 ± 6	− 157 ± 5	295 ± 7	217 ± 7	0.35 ± 0.01	76 ± 3
Pb							
Control	845 ± 13	208 ± 10	− 160 ± 6	757 ± 7	689 ± 8	0.33 ± 0.01	224 ± 2
B0-0.5	950 ± 10	163 ± 7	113 ± 2	607 ± 4	742 ± 7	0.28 ± 0.03	211 ± 5
B0-1	914 ± 23	156 ± 8	116 ± 6	579 ± 11	713 ± 12	0.28 ± 0.01	202 ± 7
B0-2	850 ± 6	143 ± 5	134 ± 4	527 ± 6	660 ± 8	0.28 ± 0.01	186 ± 2
B200-0.5	901 ± 5	163 ± 9	103 ± 8	596 ± 8	701 ± 5	0.29 ± 0.03	204 ± 3
B200-1	821 ± 7	162 ± 7	34 ± 5	590 ± 6	644 ± 3	0.30 ± 0.02	194 ± 8
B200-2	746 ± 9	148 ± 8	24 ± 3	542 ± 10	586 ± 8	0.30 ± 0.01	177 ± 2
B400-0.5	672 ± 16	106 ± 11	143 ± 8	391 ± 6	519 ± 4	0.27 ± 0.02	143 ± 3
B400-1	661 ± 8	107 ± 7	123 ± 6	394 ± 3	512 ± 10	0.28 ± 0.02	142 ± 6
B400-2	518 ± 13	93 ± 3	42 ± 5	345 ± 7	407 ± 12	0.29 ± 0.05	117 ± 3
B600-0.5	667 ± 12	81 ± 5	259 ± 10	298 ± 9	514 ± 8	0.24 ± 0.01	124 ± 2
B600-1	684 ± 9	78 ± 4	279 ± 7	291 ± 11	528 ± 9	0.23 ± 0.02	124 ± 6
B600-2	640 ± 12	68 ± 5	288 ± 8	253 ± 6	495 ± 7	0.23 ± 0.01	112 ± 3

a, R, a_e, 1/β, b, and $a \times b$ are rate constants

Values are mean ± standard errors

Control untreated soils, B0-0.5 0.5% (w/w) walnut leaves, *B0-1* 1% (w/w) walnut leaves, *B0-2* 2% (w/w) walnut leaves, *B200-0.5* 0.5% (w/w) biochar produced at 200 °C, *B200-1* 1% (w/w) biochar produced at 200 °C, *B200-2* 2% (w/w) biochar produced at 200 °C, *B400-0.5* 0.5% (w/w) biochar produced at 400 °C, *B400-1* 1% (w/w) biochar produced at 400 °C, *B400-2* 2% (w/w) biochar produced at 400 °C, *B600-0.5* 0.5% (w/w) biochar produced at 600 °C, *B600-1* 1% (w/w) biochar produced at 600 °C, *B600-2* 2% (w/w) biochar produced at 600 °C

0.5% walnut leaves, 0.5% and 2% B400, and different levels of B600 enhanced residual Zn significantly ($p < 0.05$) (Fig. 2(e)).

3.3 Correlation Between Zn and Pb Release Characteristics and Zn and Pb Fractions

A correlation study illustrated that cumulative amounts of Zn and Pb presented a positive and significant correlation with DTPA-Zn and DTPA-Pb (Table 4). Also, cumulative amounts of Zn and Pb had a negative relationship with residual fractions, but a positive correlation with exchangeable and associated oxide fractions, so greater amounts of these fractions yielded higher cumulative amounts of Zn and Pb. Higher residuals of Zn and Pb resulted in a reduction of cumulative amount and, consequently, Zn and Pb release rates. Also, the extraction capacity of DTPA-TEA was proven as an index for determining soil pollution in our previous study (Kabiri et al.,

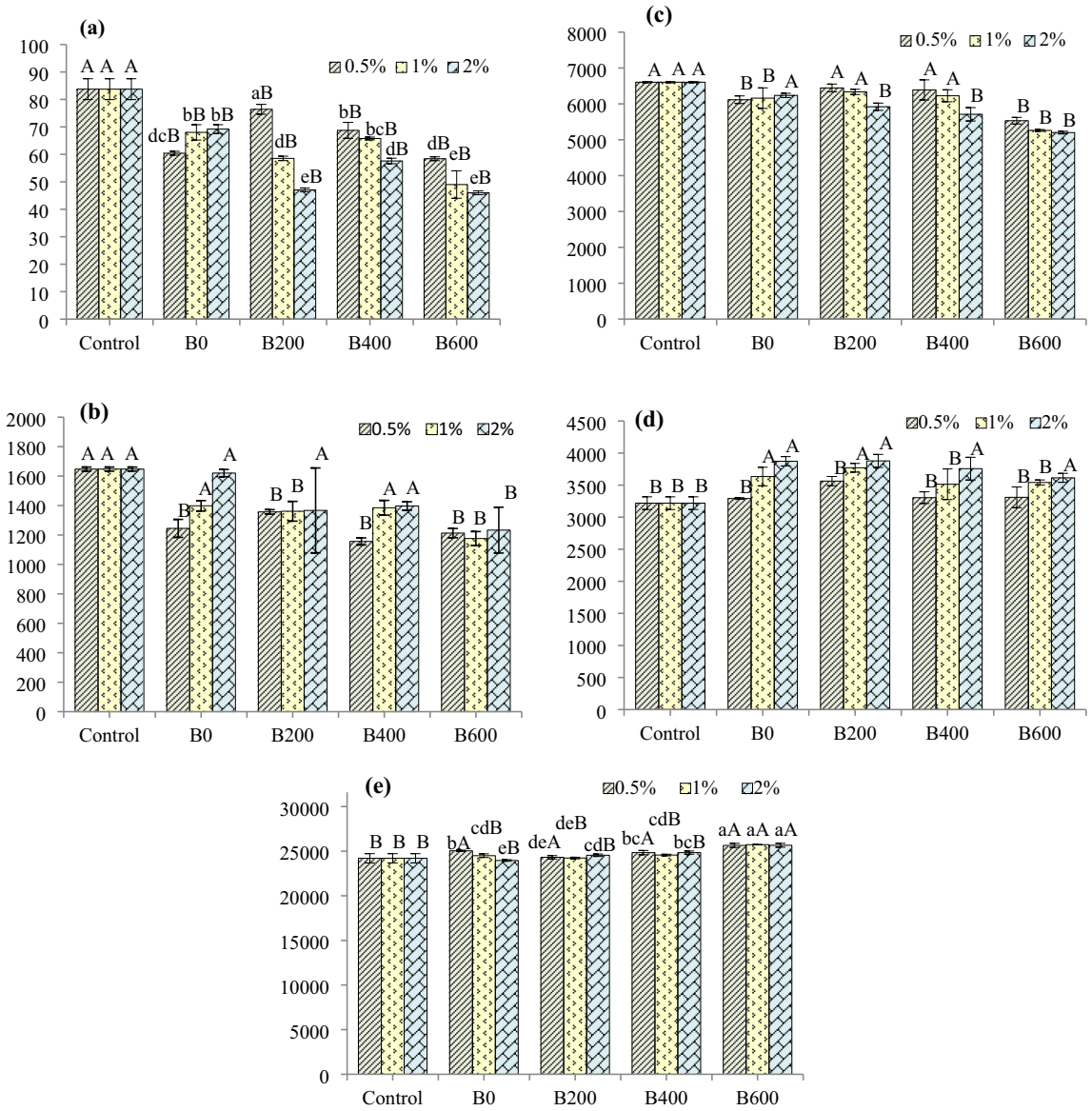

Fig. 2 The effects of pyrolysis temperatures and biochar levels interactions on fractionation of Zn (mg kg^{-1}). Different lowercase letter(s) represent significant differences between treatments by Fisher LSD's test at $p < 0.05$. Different uppercase letter(s) for each application level represent significant differences between untreated and treated soils by Fisher LSD's test at $p < 0.05$. Values are mean ± standard errors (n = 3). F1, exchangeable (a); F2, associated with carbonates (b); F3, associated with oxides (c); F4, associated with organic matter (d); F5, residual (e); B0, walnut leaves; B200, biochar produced at 200 °C; B400, biochar produced at 400 °C; B600, biochar produced at 600 °C. 0.5%, 1%, and 2%: application level of walnut or biochar

2019). So, treatments that presented a higher extractability of Zn and Pb demonstrated greater rates of Zn and Pb release.

All constants of the three equations (except for "a" of simplified Elovich for DTPA-Zn and DTPA-Pb and "a" of parabolic diffusion for DTPA-Zn) had a positive and significant correlation with DTPA-Zn and DTPA-Pb (Table 4). Therefore, higher cumulative release amounts of Zn and Pb resulted in bigger rate constants of the three equations.

The correlation analysis results (Table 4) also revealed that among fractions, exchangeable Zn and Pb and Zn and Pb associated with oxides were positive, but residuals of Zn and Pb had a negative correlation with almost all of the rate constants ($p < 0.05$ for Zn fractions and $p < 0.01$ for Pb fractions). So, treatments with lower exchangeable and Fe-Mn oxides, but higher residual fractions, diminished the rate of Pb and Zn release. Therefore, the equation constants could be used to effectively predict PTE pollution in the soil. Among the constants, "b", "$a \times b$", "R", and "$1/\beta$" were better parameters to predict the release of Zn and Pb extracted by DTPA-TEA from the control group and treatments in our experiment.

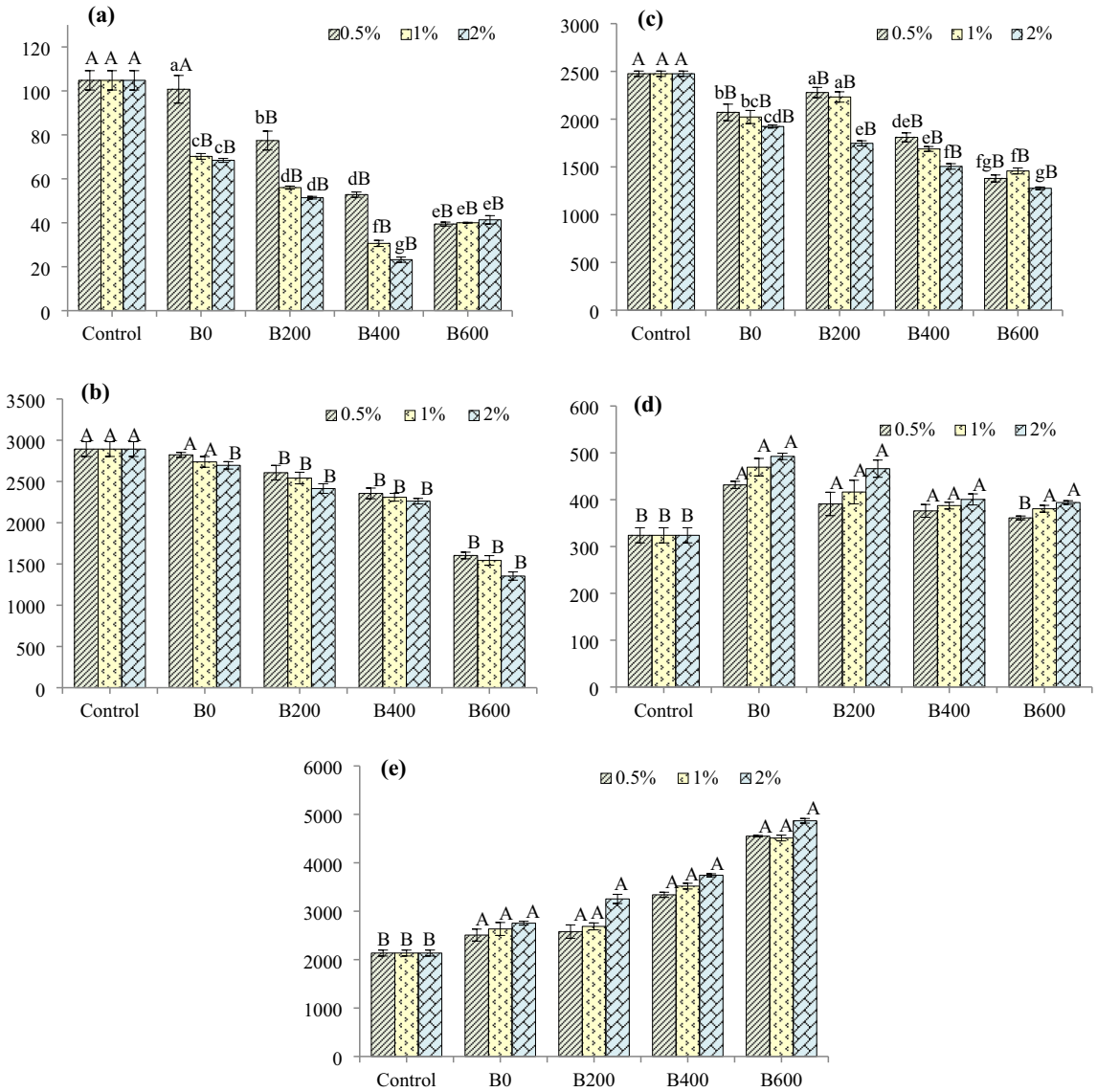

Fig. 3 The effects of pyrolysis temperatures and biochar levels interactions on fractionation of Pb (mg kg^{-1}). Different lowercase letter(s) represent significant differences between treatments by Fisher LSD's test at $p < 0.05$. Different uppercase letter(s) for each application level represent significant differences between untreated and treated soils by Fisher LSD's test at $p < 0.05$. Values are mean ± standard errors (n = 3). F1, exchangeable (a); F2, associated with carbonates (b); F3, associated with oxides (c); F4, associated with organic matter (d); F5, residual (e); B0, walnut leaves; B200, biochar produced at 200 °C; B400, biochar produced at 400 °C; B600, biochar produced at 600 °C. 0.5%, 1%, and 2%: application level of walnut or biochar

4 Discussion

The release rate of Zn and Pb is an important property of soil that determines the ability of soil to introduce metals to the solution (Sadegh et al., 2012; Zahedifar et al., 2012; Motaghian and Hosseinpur, 2013; Mohseni et al., 2018; Boostani et al., 2019). Meanwhile, biochars produced at various temperatures have different properties and could change the distribution and release kinetics of Zn and Pb from highly polluted calcareous soils. However, detailed information on the application of different biochars on the metals' release kinetics in highly polluted calcareous soils is still scanty.

The results demonstrated that the maximum release amounts of Zn and Pb were higher during the initial hours. Then, the flow rates gradually decreased during the following hours, similar to previous studies (Reyhanitabar and Gilkes, 2010; Inyang et al., 2012; Boostani et al., 2019). However, the flow rate might diffuse at first from interparticles and then from intraparticles (Siva Subramanian and Talibudeen, 1972). Biochars produced at all levels and temperatures diminished the cumulative release amounts of Zn and Pb significantly due to their available binding sites (Zahedifar and Moosavi, 2017; Sun et al., 2020). Although the most cumulative release amounts of Zn and Pb occurred after 504 h when

Table 4 Correlation coefficients (r) between Zn and Pb release characteristics and metals fractions ($n = 13$)

Metal	Release characteristics		DTPA-TEA	Fractions				
				F1	F2	F3	F4	F5
Zn	Power function	a	0.58*	0.52 ns	0.15 ns	0.64*	− 0.18 ns	− 0.47 ns
		b	0.73**	0.57*	0.69**	0.65*	− 0.11 ns	− 0.64*
		$a \times b$	0.75**	0.65*	0.33 ns	0.78**	− 0.2 ns	− 0.62*
	Simplified Elovich	a_e	− 0.88**	− 0.76**	− 0.60*	− 0.81**	0.37 ns	0.65*
		1/β	0.86**	0.74**	0.49 ns	0.86**	− 0.25 ns	− 0.70**
	Parabolic diffusion	a	0.38 ns	0.35 ns	− 0.01 ns	0.47 ns	− 0.65 ns	− 0.34 ns
		R	0.87**	0.74**	0.51 ns	0.86**	− 0.23 ns	− 0.72**
	Cumulative amount		0.86**	0.71**	0.50 ns	0.86**	− 0.2 ns	− 0.72**
Pb	Power function	a	0.91**	0.90**	0.72**	0.82**	0.32 ns	− 0.80**
		b	0.62*	0.54 ns	0.89**	0.83**	0.11 ns	− 0.88**
		$a \times b$	0.93**	0.89**	0.87**	0.94**	0.25 ns	− 0.94**
	Simplified Elovich	a_e	− 0.55*	− 0.51 ns	− 0.78**	− 0.75**	0.69 ns	0.78**
		1/β	0.89**	0.85**	0.90**	0.95**	0.17 ns	− 0.95**
	Parabolic diffusion	a	0.89**	0.87**	0.69**	0.79**	0.36 ns	− 0.77**
		R	0.89**	0.84**	0.89**	0.96**	0.16 ns	− 0.95**
	Cumulative amount		0.90**	0.86**	0.88**	0.96**	0.20 ns	− 0.95**

a, R, a_e, 1/β, b, and $a \times b$ are rate constants

F1 exchangeable, F2 associated with carbonates, F3 associated with oxides, F4 associated with organic matter, F5 residual

**Significant at $p < 0.01$. *Significant at $p < 0.05$, *ns* non-significant

no biochar was added into the soils, they declined gradually after biochar was incorporated into the treatments. The quantities of Zn and Pb decreased by 1852 mg kg^{-1} and 1908 mg kg^{-1}, respectively, when 2% B600 (the highest produced temperature and greatest level) was applied. Compared with other biochars, B600 had the biggest pH and EC, and the highest surface area. So, B600 was more effective in the redistribution of metals than other biochars. Dokht et al. (2017) studied the sorption and release of Pb in acid and alkaline soils treated with sewage sludge biochar. They reported that Pb release was 53.9%, 25.7%, and 16.8% in the control, alkaline soils treated with B350, and alkaline soils treated with B650, respectively. For acidic soils, the results were 40.4%, 27.7%, and 19.6%, respectively. Therefore, the soils treated with biochars produced at lower temperatures released more Pb than soils treated with biochars produced at higher temperatures. The researchers stated that biochars prepared at increased temperatures possessed a higher surface area, pH, aromaticity, and pores, which enhanced their capacity for PTE detoxification. Houben et al. (2013) concluded that incorporating 5% and 10% of miscanthus straw biochar reduced Zn and Pb over time. Inyang et al. (2012) reported the reduction of Pb from aqueous solutions treated with biochars. They concluded that the greatest removal of elements had been controlled by the pore diameters of biochars getting metals via precipitation, complexation, diffusion, and adsorption. Inyang et al. (2011) applied digested sugarcane bagasse and bagasse biochars in order to detoxify water from Pb. They concluded that digested sugarcane bagasse biochar removed 653.9 mmol kg^{-1}, whereas sugarcane bagasse biochar detoxified 31.3 mmol kg^{-1} of Pb from the water. They suggested that the high capacity adsorption of biochars was related to the existence of cellulose, hemicellulose, proteins, sugars, and lipid in bagasse and that their functional groups could adsorb metals. In their research, digested sugarcane bagasse biochar removed metals via precipitation, but sugarcane bagasse biochar removed the metals through surface adsorption. After investigating the adsorption and release of Cu and Pb in paddy soils cultivated for several years, Ma et al. (2010) revealed that metals were initially adsorbed by organic matter active groups. Then, they were volunteered for various soil components. In their survey, 85-year paddy soil had more organic matter than 8-year paddy soil, so this showed a higher capacity for adsorption, but a lower capability for the release of Cu and Pb.

The constants in kinetic models are indicators of the rate of Zn and Pb release from the soil. The "a", "b", and "$a \times b$" (obtained from the power function) reduced more in higher levels and prepared temperatures of biochar treatments compared with the control. In agreement with this result, Zahedifar et al. (2012), investigating the impact of feedlot cattle manure on Zn release kinetics in calcareous soils, suggested that "a"

(as a rate constant of the power function equation) was lower, but "$a \times b$" (obtained from the power function) was greater for Zn extracted by DTPA-TEA after 980 min in soil treated with 1% w/w feedlot cattle manure (0.03) compared with the control (0.02). A comparison of "$a \times b$" and "1/β" between the control and soils treated with biochar revealed that the highest value of "$a \times b$" and "1/β" was yielded in the control. However, they were reduced in this order: the soils treated with B200 > B400 > B600. So, the highest initial release of Zn and Pb occurred in the control, but the lowest was in the soils treated with B600. Therefore, considering either "$a \times b$" or "1/β", we obtained the same results in our research. Likewise, Mohseni et al. (2018) reported that the increase of "a_e" and the decrease of "1/β" (as constants of the Elovich equation for Zn and Pb) with increasing levels of sewage sludge (0%, 1%, and 3% w/w) in polluted calcareous soils. Nevertheless, some research shows that the decreases or increases in constant values are more or less different from our data. Determining the Zn release rate from some calcareous soil samples, Boostani et al. (2019) reported the range of "a_e" and "1/β" constants (derived from the simplified Elovich equation) between 0.85 and 11.4 and between 0.52 and 1.34, respectively. They defined "a_e" as the initial metal release and "1/β" as the metal release rate coefficient. In their research, the greatest flow occurred in the soil with most "a_e" and "1/β." Meanwhile, the lowest rate was for the sample possessing the least "a_e" and "1/β." However, in our study, treatments with more "a_e" and less "1/β" had a slower release rate. Sadegh et al. (2012) reported that the values of "a_e", "a", and "$a \times b$" constants increased after the addition of poultry manure in calcareous soils. The downward trend of "a_e" (derived from the simplified Elovich equation) was observed in the experiment of Zahedifar et al. (2012). As the release rate of Zn and Pb decreased in treatments with higher levels and temperatures of biochars, smaller values of "R" were obtained as well. In a research performed by Motaghian and Hosseinpur (2013) on some sewage sludge-treated soils, "a" and "b" as Zn release kinetic parameters were obtained between 3.3 and 5.0 mg kg^{-1} h^{-1} and between 0.19 and 0.24 (mg $kg^{-1})^{-1}$. They determined "R" and "1/β" as between 0.52 and 0.73 mg kg^{-1} $h^{-1/2}$ and between 1.4 and 2.1 mg kg^{-1} h^{-1}, respectively. In their study, similar to our research, lower Zn release from the soils resulted in lower values of "R." Furthermore, regardless of "1/β" (which, in our study, had smaller values in treatments with a lower release, but in the research of Motaghian and Hosseinpur (2013) had bigger values), other parameters of all equations in our research and their experiment decreased similarly as a result of the metals' release reduction rate. To investigate the Zn release characteristics in 10 calcareous soil samples with Zn ranging from 74.6 to 125.5 mg kg^{-1}, Hussain et al. (2011) applied DTPA to extract Zn over 24 h. The parabolic diffusion equation narrated the best model for the release of Zn in their experiment. These researchers calculated "R" by 0.09 to 0.51 for all experimental soils. So, the range of "R" was greater in our research than in the previous studies mentioned above. This is probably due to much higher metal content and different metal distribution in the soil.

There was a significant correlation between "a" (constant of the power function) and DTPA-extractable Zn and Pb. Similar to our results, Reyhanitabar and Gilkes (2010) demonstrated a significant correlation between "a" (constant of the power function equation) and DTPA-extractable Zn. In our study, "a_e" (rate constant of the simple Elovich equation) had a negative correlation with DTPA-extractable Zn and Pb, but "1/β" (rate constant of the simple Elovich equation) yielded a positive correlation with DTPA-extractable Zn and Pb. However, in the experiment of Zahedifar et al. (2012), both rate constants of the simple Elovich equation ("a_e" and "1/β") had positive correlations with DTPA-Zn concentration. Also, Motaghian and Hosseinpur (2013) found significant positive correlations between "a" and "$a \times b$" (derived from the power function equation in bulk soil and rhizosphere) and "a_e" (only in bulk soil) and "1/β" (in bulk soil and rhizosphere) obtained from the simple Elovich equation, as well as "a" and "R" (of parabolic diffusion in bulk soil and rhizosphere) with Zn extracted by DTPA-TEA. Concordant to Motaghian and Hosseinpur (2013), in our research, "a" (of parabolic diffusion) correlated positively with DTPA-Pb content, and also "R" correlated positively with both extracted Zn and Pb by DTPA. Contrary to their research, our results revealed that "a" (of parabolic diffusion) did not correlate with DTPA-Zn. However, Mohseni et al. (2018) asserted that there was a significant positive correlation between "a" and "$a \times b$" (constants of the power function equation) as well as between "a_e" and "1/β" (constants of the simple Elovich equation) ($p < 0.05$) with DTPA-Zn. Moreover, there was a significant positive correlation between "a", "b", and "$a \times b$" (parameters of the power function equation) and also "a_e" (parameter of the simple Elovich equation) with DTPA-Pb. The cumulative amount of Zn and Pb elucidated significant correlations with DTPA-extractable Zn and Pb, which was similar to the research by Motaghian and Hosseinpur (2013). They obtained significant positive correlations between cumulative amounts of Zn and Zn extracted by DTPA-TEA from bulk soil and rhizosphere. Therefore, according to our correlation study and previous research, "b", "$a \times b$", "R", and "1/β" were more feasible and pragmatic for describing metal release.

Our investigation showed that the cumulative amount and rate of Zn and Pb, extracted by DTPA, decreased in the soils treated with larger levels of biochar produced at higher temperatures because biochars typically exhibited a highly toxic metal adsorption capacity. Yildiztugay (2019) reported that biochar could minimize oxidative damages in wheat under Co stress. Cui et al. (2019) documented that the application of 5% or 15% biochar could change the metals'

distribution to phases that were rarely available. So, the incorporation of biochar could reduce the release kinetics of metals in the soil by improving the distribution of metals to barely accessible sites. Thus, the larger levels of biochar produced at higher temperatures diminished metals in the forms of exchangeable, carbonate, Fe-Mn oxides, and enhanced metals trapped in organic matter and residual fractions. According to the results, which are similar to our previous study, biochars would alter the metals' distributions in a way that they declined readily available forms (exchangeable, associated with carbonates, and associated with Fe-Mn oxides), but raised less reachable sites (associated with organic matter and residuals) in the soil (Kabiri et al. 2019). Similarly to the present research, Karimi et al. (2020) reported that the application of 2% corn residue biochar produced at 500 °C decreased DTPA-Zn in a calcareous soil. In other work, Karimi et al. (2019) reported that the application of corn residue biochar produced at 500 °C increased Zn associated with organic matter and residual fraction in calcareous soil, while exchangeable and associated with Fe-Mn oxide fractions decreased. They reported that the application of corn residue biochar produced at 500 °C increased the Zn associated with Fe-Mn oxides when compared with the control. They concluded that the increases in the Zn associated with Fe-Mn oxides in soil treated with the biochar produced at 200 °C affected by increasing the ligand adsorption onto the oxide surfaces. Therefore, the amounts of Zn and Pb released decreased more when the soil samples were treated with greater levels of biochars prepared at higher temperatures. In our experiment (as was suggested by Marschner (1995)), most of the Zn fractions found as residual > associated with Fe-Mn oxides > associated with carbonates. In the study conducted by Hussain et al. (2011), the distribution of Zn relative proportion among soil components was in the same descending order of our study (Fig. 2(a–d)). They reported that Fe-Mn oxides were the major components that governed Zn release. Similarly to our results, Bogusz and Oleszczuk (2020) observed a reduction in fractions F1–F3 and an increase in F4 for Pb (Fig. 1(b)). They attributed the possible reasons for the great affinity of Pb to biochar. Sun et al. (2020) stated that biochar transferred Pb from the surface to deeper layers by changing fractions to residual. In comparison with the control, with an increase in the addition of biochar, the detachment of heavy metals slowed down. Kołodyńska et al. (2017) suggested that the main mechanism of adsorption is the exchange of electrons between metals (Cu(II), Zn(II), Cd(II), Co(II), and Pb(II)) and manure-derived biochar. According to their results, contact time reduced the adsorption rate, and so did biochar's occupied sites. Investigating the adsorption of Pb(II) on the bagasse biochar, Ding et al. (2014) shared similar results.

In our experiment, a negative relationship was revealed between the total organic carbon (TOC) of biochars with the cumulative release of Zn (− 0.76) and Pb (− 0.72) ($p < 0.01$). This demonstrated that one of the main adsorption mechanisms of Zn and Pb on biochars was complexation with organic groups (pyrone, pyridine) (Bogusz et al. 2017). Also, a negative relationship between the surface area (S_{BET}) of biochars with the cumulative release of Zn (− 0.81) and Pb (− 0.84) ions was observed ($p < 0.01$). This stated that increases in the surface area (S_{BET}) of biochars led to a decrease and increase in desorption and adsorption of both metals, respectively.

The data presented in our research also revealed that the release of Zn differed from Pb (Fig. 1(a–b)). The amount of cumulative release for Zn was more pronounced in comparison with Pb during 2–504 h in soils treated with biochars. In other words, biochars could adsorb more Pb than Zn. The varied release of Zn and Pb indicate that metal behavior in the soil is largely determined by the distribution in soil. In our study, probably the most supportive evidence for the difference in released amounts of metals referred to their fractions content. According to our results, the sum of Pb content existed as exchangeable, carbonates, and organically bounds was calculated as 69% of pseudo-total Pb content. Meanwhile, Zn was distributed by 23% of pseudo-total Zn content in these fractions, which possessed weaker bounds and dissociated Zn and Pb substantially faster than organically and residual bounds (totally 77 and 31% of Zn and Pb pseudo-total content, respectively) (Figs. 2 and 3). Also, greater levels and production temperatures of biochars incorporated in treatments could lead to more Pb being absorbed than Zn. Therefore, the release of Zn occurred more extensively in comparison with Pb for soils treated with higher levels and temperatures of biochars. Furthermore, Pb^{2+} (1.20) was characterized by having a bigger ionic radius than Zn^{2+} (0.74). Hence, the hydrated radius of Pb^{2+} was smaller than that of Zn^{2+} (Li 2006; Bogusz et al. 2017; Sun et al. 2020). In addition, the electronegativity of Pb^{2+} (1.8) is higher than that of Zn^{2+} (1.6). Therefore, the interactions of Pb^{2+} with the surface of biochars were stronger than that of Zn^{2+}, so Zn released its ions from the surface of biochars more rapidly than Pb (Bogusz et al. 2017). Xu et al. (2013) concluded that the major adsorption mechanism is complexation and among four experimental metals (Pb > Zn > Cd > Cu), Pb revealed the strongest complexation with $-O^-$ in biochar phenolic-OH, because Pb^{2+} characterized greatest ionic potential (Pb(0.22) > Zn(0.16) > Cd(0.14) > Cu(0.10)) among other metals (Petrov et al. 1992). Other researchers have demonstrated that Pb is adsorbed on biochar better than other heavy metals (Ahmad et al. 2018).

5 Conclusions

The present study showed that the cumulative amount of Zn and Pb extracted by DTPA and the release rate of these metals

from soil solid phases to soil solution decreased with increasing biochar level and pyrolyzing temperature of biochar production. The amount and rate of Zn and Pb extracted by DTPA are strongly related to the metal distribution in solid phases of soil. Meanwhile, promoting the transfer of readily free forms (exchangeable, associated with carbonates, and associated with Fe-Mn oxides) to tightly bound partitions (associated with organic matter and residual), biochars could lessen the migration of Zn and Pb from the solid phase to a soil solution. Therefore, the results illustrated that the application of 2% biochar produced at 600 °C could stabilize and reduce the release rate of Zn and Pb from highly polluted calcareous soils to the solution.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflicts of interest.

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