Kinetic and Equilibrium Studies on the Zinc Adsorption-desorption Characteristics of Some Promising Biochars in Aqueous Solutions

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Title Page

Kinetic and equilibrium studies on the zinc adsorption-desorption characteristics of some promising biochars in aqueous solutions

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A concise and informative title:

Biochar effects on the zinc adsorption-desorption in aqueous solutions

Kinetic and equilibrium studies on the zinc adsorption-desorption characteristics of some promising biochars in aqueous solutions

Abstract

The present research aimed at investigating zinc (Zn) sorption capacity of the biochars derived from apple wood (WB) and rice straw (RB) feedstocks at two 300 and 600 °C pyrolysis temperatures (WB300, WB600, RB300 and RB600, respectively) in aqueous solutions. Kinetic and equilibrium sorption experiments were conducted via batch technique. In equilibrium adsorption experiments, the study used the concentration range of 5-200 mg Zn L⁻¹ and focused on the solution pH effect on Zn adsorption in biochars under the following conditions: unadjusted and adjusted pH (4 and 6) and three ionic strength levels (0.01, 0.03, 0.1 M KNO₃). Zinc desorption experiments were conducted under all above mentioned conditions but without pH adjustment at five separate stages. Kinetic data analysis indicated that Zn adsorption in biochars reached the near steady state within 24 hours with the sorption rate order of WB300 < WB600 < RB300 < RB600. The best fitness was superior to both Elovich and exponential rate models. Also, Zn adsorption isotherms in the studied biochars were shown to fit quite well to Langmuir, Freundlich and Dubinin-Radushkevich models. Zn sorption maxima were found to be 4.3, 16.4, 17.9 and 33.3 mg g⁻¹, on average, for WB300, WB600, RB300, and RB600, respectively. The initial increased pH solution from 4 to 6 caused an increase in Zn adsorption in RB600, RB300 and WB600, however the sorption maxima in WB300 was detected at pH 4. The rise in solution ionic strength from 0.01 M to 0.1 M dropped the Zn adsorption capacity in all the studied biochars. Findings suggested that rice straw derived biochars showed a better performance than woody biochars in Zn sorption and retention from aqueous solutions. In addition, this ability increased with increasing pyrolysis temperature in both types of biochars. Finally, the study revealed that rice straw biochars, produced at high pyrolysis temperatures, can serve as economical and efficient absorbents for Zn removal from aqueous solutions.

Keywords: Adsorption, Biochar, Desorption, Ionic strength, pH, Zinc

1. Introduction

Biochars are porous, fine-grained, pyrolyzed biosorbents derived from plant and animal residues in oxygen-limited conditions (Shackley et al., 2012). Characteristics and applications of these environment-friendly materials are dictated mainly by variations in feedstock type and pyrolysis conditions. As the pyrolysis temperature rises, the organic substances evaporate or decompose which leads to a higher ash content. This is closely associated with pH rise in response to increased content of alkali and alkali earth carbonates and oxides. This may be the result of the decreased functional groups such as -COOH (Jin et al., 2016).

The decision to apply the effective sorbent for heavy metals depends on adsorption rate and capacity, mechanical strength, and economical efficiency. Though activated carbon meets all the requirements, it is hardly a favorable choice due to high production costs. Here, biochar can be a good alternative because of low-cost and simple production technology. Biochar surfaces are less carbonized and contain more oxygen-containing groups compared to activated carbon. However, its adsorption capacity for heavy metals varies depending on biomass type and pyrolysis conditions as well as the heavy metal type (Ni et al., 2019). Many studies indicate that biochars derived from agricultural wastes can be used as an appropriate sorbent for heavy metals in soil and water systems because of high specific surface area and abundant oxygen-containing functional groups as well as high precipitating anions (Park et al., 2016; O'Connor et al., 2018). It should be noted that metal adsorption on biochar surfaces is determined by pH level. In pH < pH_{PZC}, most functional groups with positive charge can adsorb anions, while in pH_{PZC} < pH, their negative charge can easily adsorb cations (Abdel-Fattah et al., 2015). Biochar-based sorption mechanisms of metals from solutions include electrostatic interaction between the heavy metals and biochar surface, cation exchange between metals and protons or between alkaline cations on biochar surface, complexations between metals and functional groups and π electrons on the aromatic structure of biochar, and metal precipitation (Cui et al., 2016). Studies confirm that metal sorption mechanisms may be attributed to biochar characteristics such as ash concentration, specific surface area and zeta potential value, all of which are appropriate in the case of heavy metals (Ding et al., 2016).

Zinc (Zn) is a heavy metal with toxic properties in high concentrations, but it is essential nutrient to plant growth in low concentrations. There is not a wealth of literature on Zn sorption mechanisms by biochar; however, it would be possible to focus on precipitation with oxyanions such as PO₄³⁻ and CO₃²⁻, ion exchange with metals like K⁺, Na⁺, Ca²⁺ and Mg²⁺, surface complexation with oxygen-containing functional groups such as -COOH and -OH, and dative bond with π electrons of C=C and C $\equiv$ C in aromatic complexes as possible mechanisms (Li et al., 2017). Heavy metal adsorption capacities may vary depending on biochar type. For instance, Zn sorption capacity in biochars derived from pig and cow manures is reported to be 50-81 mg g⁻¹; however, the respective value for Cu, Cd and Pb are 75-95, 80-122 and 154-230 mg g⁻¹ (Kolodyńska et al., 2012). Chen et al. (2011) quantified the Zn sorption capacity of wood derived biochar at 6.8 mg g⁻¹ in aqueous solutions, but this rose to 12.5 mg g⁻¹ when corn straw derived biochar was used. In another study, Frišták et al. (2015) reported the sorption capacity of 0.9-2.2 mg g⁻¹ for biochars derived from beech wood chips and garden green wastes. Those derived from sesame straw and pyrolyzed at 700 °C biochar indicated a Zn sorption maxima

of 34 mg g⁻¹ (Park et al., 2016). According to Abdelhadi et al. (2017), the biochar derived from olive solid waste at 350 °C pyrolysis temperature exhibited an 80 percent cumulative removal capacity for Cu, Pb, Cd, Ni and Zn in solution systems. Van Hien et al. (2020) reported that the Zn sorption rate followed the order of rice husk < wood < bamboo as biochar sources, where the bamboo with the sorption capacity of 12.5 g L⁻¹, accounted for 96% Zn removal in the solution with the initial concentration of 80 mg L⁻¹. Zhao et al. (2020) found that the sorption capacity of biochars from rice husk, chicken manure, and sewage sludge for Pb was higher than that for Zn. The study suggested that Zn sorption in biochars can greatly depend on the nature of feedstock biomass.

With this background in the literature, the present study aimed at deriving biochars from rice straw in Northern Iranian Province, and wood chips from apple tree pruning as part of agricultural and garden waste in Northwest of Iran. Heavy metal sorption-desorption reactions in the environment are crucial processes upon which Zn retention depends. The main objectives of this study are as follows:

- 1) Assessing the impact of biomass type and pyrolysis temperature on physical and chemical properties of the derived biochars;
- 2) Assessing the derived biochars in Zn sorption-desorption and determining pH and solution ionic strength effects on the biochar's sorption capacity; and
- 3) Obtaining kinetic and isotherm parameters from Zn sorption-desorption experiments.

2. Materials and methods

2.1. Preparation of biochars

Biochars used in this study were derived from apple wood and rice straw feedstocks. The former was gathered from the apple orchards around Urumia and the latter from paddies around Rasht, respectively in Northwest and North of Iran. After collection, the biomass samples were washed with water and air-dried, then crushed and sieved to <1 mm particles. Slow pyrolysis technique was employed inside an oxygen-limited electrical furnace with argon flow rate of 2.5 L min⁻¹. The furnace was programmed to provide the pyrolysis temperatures to 300 and 600 °C at a rise rate of 10 °C min⁻¹. The maximum temperatures was held for one-hour (Cui et al., 2016). Then, the furnace was turned off and the produced biochars were cooled down to reach ambient temperature. The biochars derived from apple wood and rice straw at 300 and 600 °C pyrolysis temperatures were labeled WB300, and WB600, RB300 and RB600, respectively.

2.2. Characteristics of biochars

First, the biochar samples were dried in the oven at 105 °C for 2 hours. Then, they were subjected to combustion in the furnace at 750 °C for 6 hours and the ash content was calculated by measuring the ratio of ash weight to the total biochar weight (Al-Wabel et al., 2013). The pH and EC values of the biochars were measured at a 1:10 ratio (biochar to distilled water) after shaking for 30 minutes (Lee et al., 2013). Carbon (C), hydrogen (H), and nitrogen (N) concentration of the biochars were determined using CHNS Analyzer (Elementer, Vario EL III), and the oxygen content was calculated in terms of weight difference ($100 - \sum(C + H + N + S + \text{ash}) \text{ percents}$). In order to obtain the total concentration of other elements in the biochar, dry ashing method was used (Westerman, 1990). P and K concentrations were measured by spectrophotometer (Philler Scientific, SU6100) and flame photometer (Model Corning, 410), respectively. The concentrations of Ca, Mg, Fe, Zn, Cu and Mn were analyzed using atomic absorption spectrometer (Shimadzu, AA-6300). Functional groups were assessed using Fourier-transform infrared spectroscopy (FTIR) (Bruker, Tensor 27), and the morphology and microstructure of the produced biochars were investigated using scanning electron microscope (TESCAN, MIRA3FEGSEM). Specific surface area of the biochars was measured based on standard BET method using N₂ gas sorption-desorption isotherms. To determine point of zero charge (pH_{pzc}), the authors employed mass titration method as described by Noh and Schwarz (1990). Acidic functional groups on biochar surfaces were also identified through Bohem titration (Tsechansky and Graber, 2014). Also, biochar cation exchange capacities (CECs) were evaluated by extracting the biochars with 1M sodium acetate solution at pH 7.

2.3. Adsorption and desorption isotherms

Zn adsorption-desorption experiments were conducted using the batch technique. For this, Zn solutions were prepared by dissolving zinc nitrate (Zn (NO₃)₂·6H₂O) and potassium nitrate (KNO₃) in distilled water. Kinetic adsorption experiments were conducted in 50 mL centrifuge tubes using 0.1 g duplicate subsamples of each biochar in 20 mL background electrolyte solution (0.03 M KNO₃) containing 200 mg Zn L⁻¹, without pH adjustment. The tubes were agitated on a shaker at 120 ± 5 rpm and 25 ± 1 °C for contact times of 0.5, 1, 2, 4, 8, 12, 16, 24, 32, 48 and 64 hours. Then, the tubes were centrifuged at 6000 rpm for 10 minutes and the supernatant was filtered through a Whatman filter. The concentration of Zn in solution was measured by Atomic absorption spectrophotometer (Shimadzu AA-6400). Isotherm experiments were conducted in 50 mL centrifuge tubes containing 0.1 g of duplicate subsamples of each biochar in 20 mL background electrolyte solution (at three levels of ionic strength 0.01, 0.03, and 0.1 M of KNO₃) containing

different initial Zn concentrations (5, 10, 20, 40, 60, 80, 100, 150, 200 mg L⁻¹) with three initial pH values (unadjusted pH, adjusted pH at 4 and 6) adjusted by 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH solutions. The reaction mixture was shaken at 25±1 °C for 24 hours. After reaching equilibrium, the tubes were centrifuged at 6000 rpm for 10 minutes and the supernatant was filtered and analyzed for Zn concentration. The adsorption amount (q_e, mg g⁻¹) and removal efficiency were calculated according to Equation 1 and Eq. 2: (Wang et al., 2015).

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where, C_i and C_e are initial and equilibrium concentrations (mg L⁻¹), respectively; m stands for biochar weight in terms of g, and V is the volume of solution (L).

Desorption experiments were conducted at the end of adsorption experiments. For this, the initial Zn concentration of 200 mg L⁻¹ at all levels of ionic strength under unadjusted pH condition was employed. At the end of adsorption experiment, 15 mL of supernatant was removed and 15 mL of background solution (0.03, 0.01, and 0.1 M KNO₃) was added to the tubes. The tubes were shaken for the equilibrium time and then centrifuged. A total of five desorption stages were accomplished. Finally, the amount of desorbed Zn at each stage was calculated by applying equation (1), in which C_i is the initial concentration in each desorption stage that is obtained through dividing the final concentration (C_e) of the preceding stage, by the degree of dilution resulting from adding the background solution (Yang et al., 2018). Total desorption efficiency was derived from the following equation:

$$\text{Desorption efficiency} = \frac{q_{\text{des}}}{q_{\text{ads}}} \times 100 \quad (3)$$

Where q_{ads} is the amount of adsorbed Zn and q_{des} stands for Zn desorbed.

2.4. Models of adsorption kinetic and isotherm

Pseudo first-order, pseudo second-order, parabolic diffusion, exponential and Elovich models were tested for their suitability to describe the kinetics of Zn sorption by studied biochars (Table 1). Additionally, the Freundlich, Langmuir and Dubinin-Radushkevich models were employed to fit the adsorption results.

Polanyi potential (ε) in Dubinin-Radushkevich equation can be obtained from Eq. (4):

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (4)$$

where, R is universal gas constant (0.008314 kJ mol⁻¹ °K⁻¹), T is temperature (°K) and C_e is equilibrium concentration in the solution (mg L⁻¹).

In the Dubinin-Radushkevich model, K_D is used for calculating mean free energy (E = 1/√2K_D). If E is less than 8 kJ mol⁻¹, physical adsorption is assumed, but if its value occurs in the range of 8 to 16 kJ mol⁻¹, then the assumed adsorption type will be chemical (Chabani et al., 2006).

Table 1. Kinetic and isotherm models used in this study.

Model	Equation	Parameters
Pseudo-first order	$q_t = q_e(1 - \exp(-k_1 t))$	k ₁ : adsorption rate constant (hour ⁻¹)
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	k ₂ : adsorption rate constant (mg ⁻¹ g hour ⁻¹)
Parabolic diffusion	$q_t = q_0 - k_p t^{\frac{1}{2}}$	k _p : diffusion rate constant (mg ^{-0.5} g ^{0.5})
Exponential	$q_t = at^b$	a: initial adsorption rate constant (mg g ⁻¹ hour ⁻¹) b: adsorption rate coefficient ((mg g ⁻¹) ⁻¹)
Elovich	$q_t = \frac{1}{B} \ln(aBt + 1)$	a: initial adsorption rate constant (mg g ⁻¹ hour ⁻¹) B: adsorption constant (mg ⁻¹ g)
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K _F : relative adsorption capacity (mg g ⁻¹) n: intensity of adsorption
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q _m : maximum adsorption capacity (mg g ⁻¹) K _L : Langmuir constant (L mg ⁻¹)
Dubinin-Radushkevich	$q_e = (q_m') \exp(-K_D \varepsilon^2)$	q _m ': maximum adsorption capacity (mg g ⁻¹) K _D : constant related to the adsorption energy (mol ² KJ ⁻²) ε: adsorption potential (kJ mol ⁻¹)

q₀, q_t and q_e are the amount of Zn sorption (mg g⁻¹) at time zero, t and at equilibrium condition, respectively, C_e is the equilibrium concentration in the solution (mg L⁻¹).

A relatively high value of the coefficient of determination (r^2) and low value of the standard error of estimate (SEE) were used as the criterion for the best-fit equations for kinetic and isotherm data. The standard error of estimate was calculated using Excel software as follows:

$$SEE = \left[\frac{\sum (q - q')^2}{n-2} \right]^{0.5} \quad (5)$$

where q and q' are the measured and calculated adsorption capacity, respectively, and n is the number of measurements. GraphPad Prism 8 software was used for calculating the kinetic and isotherm equation parameters as well as the values of determination coefficient (r^2) via non-linear regression method.

3. Results and discussion

3.1. Physicochemical properties of biochars

Properties of the biochars produced in this study are presented in Table 2. The ash concentration of RB300 and RB600 were higher than those of WB300 and WB600. The high ash content of rice straw biochars resulted from accumulation of various inorganic components during pyrolysis. Comparisons indicate that pH values of rice biochars were higher than those of woody biochars which in turn supports a close association between pH and elemental composition of biomass (Lie et al., 2017).

As expected, the higher the pyrolysis temperature, the higher the EC value, which can be attributed to high levels of soluble salts containing K^+ ions (Reyhanitabar et al., 2020).

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Table 2. Physicochemical characteristics of the studied biochars.

Property		Biochar			
		WB300	WB600	RB300	RB600
Ash (%)		6.7	11	16	23
pH		5.3	8	6.3	9.6
EC (dS m ⁻¹)		0.331	1.2	2.8	5.6
C (%)		62.63	66.69	44.48	51.92
N (%)		0.68	0.52	1.56	1.33
H (%)		3.06	1.99	2.38	1.65
O (%)		26.93	19.80	35.58	22.1
H/C*		0.58	0.36	0.64	0.38
O/C*		0.32	0.22	0.60	0.32
CEC (cmol _c kg ⁻¹)		88.17	59.65	106.85	82.95
S _{BET} (m ² g ⁻¹)		1.93	147.66	7.79	81.58
pH _{PZC}		4.10	6.75	6.20	9.35
Functional groups (mmol g ⁻¹)	Carboxylic	0.15	0.09	0.25	0.07
	Lactonic	0.11	-	0.11	0.18
	Phenolic	0.08	0.20	0.30	0.12
P (g kg ⁻¹) **		0.22	1.26	1.38	2.51
K (g kg ⁻¹)		2.85	11.09	36.54	68.41
Ca (g kg ⁻¹)		2.86	6.50	17.46	23.48
Mg (g kg ⁻¹)		0.74	1.04	4.03	7.41
Fe (mg kg ⁻¹)		88.4	495.43	489.17	912.65
Zn (mg kg ⁻¹)		13.0	32.89	22.14	58.91
Cu (mg kg ⁻¹)		22.98	71.50	37.77	87.78
Mn (mg kg ⁻¹)		36.54	97.2	43.50	91.08

* Molar ratio ** P, K, Ca, Mg, Fe, Zn, Cu and Mn refer to total concentration of the respective elements.

As for CEC, at both pyrolysis temperatures, the CEC of wood based biochar was lower than that of rice based biochar and a rise in pyrolysis temperature caused a drop in CEC, which is supported in the literature (Cely et al., 2015). The rise in pyrolysis temperature led to a decrease in O/C ratio, and an increase in aromatic compounds eventually causing CEC decline. CEC can be a criterion for assessing the contribution of ion exchange mechanism in Zn sorption. On the other hand, a decrease in CEC in the case of WB600, and RB600 probably indicates a lower importance of ionic exchange in Zn sorption by these biochars as compared to WB300 and RB300. Higher O/C molar ratio in RB300 and WB300 confirms that there are more polar functional groups and higher surface hydrophilicity in these biochars. Specific surface area in both type of grass- and wood-based biochars were linked with the rise in pyrolysis temperature, ultimately resulting in increasing channel structures. However, the rate of increase in specific surface area was higher in woody biochars. This,

too, is in line with the earlier studies (Reyhanitabar et al., 2020). Concentration of all the assessed elements increased with pyrolysis temperature in both feedstock types. Also, for rice derived biochars the corresponding amounts exceeded those of woody biochars.

Figure 1. Scanning electron micrographs of WB300, WB600, RB300 and RB600.

As can be seen in Figure 1, a higher pyrolysis temperature enhances volatilization of organic compounds and formation of new porous structure that justifies increase in specific surface areas. EDS analyses (Figure 2) show that rice biochars compared to woody biochars contained more Si. Additionally, the rice biochars demonstrated Al peak which is because of high uptake of this element by rice, but in woody biochars, P peak was observed instead. These elements can be effective in Zn sorption by biochars.

Figure 2. EDX spectra of WB600 and RB600 after Zn sorption, at initial Zn concentration of 200 mg L⁻¹.

FTIR analysis of the biochars (400–4000 cm⁻¹) at pre- and post-Zn sorption is shown in Figure 3. Usually as the pyrolysis temperature rises, complexities in FTIR peaks decrease. The band appears around 1100 cm⁻¹ had a high intensity in rice biochars, while lower intensity was detected in woody biochars, chiefly limited to ether C–O-stretching vibrations. However, the peak declined after Zn sorption. Surface functional groups such as carboxyl and hydroxyl acting as proton-donor or deprotonating agents involved in a covalent bond with Zn ions disappeared or lost their intensities (Samsuri et al., 2014). Stretching vibrations seen in the range of 2950 cm⁻¹ are associated with –CH₂–/–CH₃ in aliphatics and alicyclics. This peak decreased or disappeared after Zn sorption on the studied biochars. Heavy metal bond with carbon (M–C bond) in these groups could be a metal-methylidin (MC), metal-methylin (MCH), or metal-methyl bonds depending upon the ligand attached to the carbon atom (Thirumavalavan et al., 2011).

Figure 3. FTIR spectra of WB300, (a) WB600, (b) RB300, (c) and RB600 (d) before and after Zn sorption, at initial concentration of 200 mg L^{-1} .

3.2. Kinetics of adsorption

Zn adsorption on the studied biochars was a function of time and increased with time from 30 minutes to 24 hours (Figure 4). The sorption increased rapidly up to about 24 hours, beyond which a near steady-state condition was attained. Estimated Zn adsorption maxima were roughly 3.89, 16.32, 18.80 and 33.46 mg g^{-1} in WB300, WB600, RB300 and RB600, respectively. The time spent to reach equilibrium state was shorter in WB300 than for other investigated biochars. Initial rapid adsorption is attributed to the surface adsorption of Zn ions on macropores and outer surfaces. These binding sites decreased with time and the adsorption entered the decelerated stage. Slow stage can be due to adsorption in micropores and the re-distribution of Zn ions from outer to inner surfaces (Ahmad et al., 2014; Betts et al., 2013).

Figure 4. Adsorption kinetics of Zn by different biochars used in this study.

According to the surface area values (Table 2) and the pore structure of the studied biochars (Figure 1), it can be claimed that Zn adsorption on WB300 occurs in outer surfaces and some macropores, whereas in the others, inner surfaces and micropores are also involved in Zn sorption. For times up to 64 hours, Zn sorption was the highest for RB600 and the lowest for WB300, while almost similar for RB300, WB600.

Different equations were tested for their suitability to describe the kinetics of Zn sorption by the studied biochars. The range, mean r^2 (coefficient of determination) and SEE (standard error of estimate) values appear in Table 3. The results revealed that r^2 , in best fit equations follows the order Elovich > exponential > pseudo second-order > parabolic diffusion > pseudo first-order. A look at the two models of Elovich and exponential proved to be more adequate in accounting for the process than the other models. Furthermore, it had highest r^2 , and the least SEE. The average values of r^2 and SEE were 0.97, 0.72 for the Elovich model and 0.95 and 0.5 for the exponential model, respectively. Good fit of the Elovich model in Zn sorption on biochar derived from meat and bone meal have been previously reported (Betts et al., 2013). The constant “a”, that is a measure of the initial adsorption rate, for Elovich and exponential models for the four studied biochars was in an order of WB300 < WB600 < RB300 < RB600 (Table 4).

Table 3. Range and mean values of the coefficient of determination (r^2) and standard error of estimate (SEE) for the kinetics models used in this study.

Model	r^2		SEE	
	Range	Mean	Range	Mean
Pseudo-first order	0.67-0.93	0.80	0.35-3.48	1.78
Pseudo-second order	0.89-0.98	0.93	11.93-50.83	26.80
Parabolic diffusion	0.78-0.83	0.81	0.55-2.72	1.78
Exponential	0.93-0.96	0.95	0.33-1.49	1.05
Elovich	0.97-0.98	0.97	0.17-1.06	0.72

Since the Elovich model was developed on the basis of the chemical sorption on heterogeneous surfaces, one may argue that chemical bonds may have formed when Zn ions were adsorbed on heterogeneous surfaces of biochars. Elovich model addresses biphasic reactions in which the initial adsorption rate is high and then continues slowly, which has been observed in similar reactions and suggests a limited adsorption reaction by diffusion (Betts. et al., 2013). Cheung et al. (2000) described Zn and Cu sorption by biochar based on Elovich model inferring that adsorption rate is limited by diffusion via Biochar pores.

Figure 5. Zn sorption data for the studied biochars (a) the fitting of Elovich equation, (b) the fitting of exponential model. q_t is the amount of Zn sorption (mg Zn g^{-1}) at time t .

Table 4. Values of Elovich and exponential equation coefficients for Zn sorption by the studied biochars.

Biochar	Elovich				Exponential			
	$\ln a$	B	r^2	SEE	a	b	r^2	SEE
WB300	1.63	1.34	0.98	0.17	1.74	0.24	0.96	0.33
WB600	4.21	0.41	0.97	0.84	8.71	0.18	0.93	1.23
RB300	4.52	0.37	0.98	0.83	10.07	0.18	0.94	1.14
RB600	7.19	0.28	0.97	1.06	21.55	0.13	0.96	1.49

Note: For units refer Table 1

3.3. Adsorption isotherms

Isotherm curves indicate that as the equilibrium concentration increases, Zn adsorption in biochars drops and the slope of the curve decreases which can be due to heterogeneous compounds in the sorption sites with different binding energy

295 levels (Figure 6). Comparison of the shape of sorption isotherms in the studied biochars (Figure 6) showed the steep initial
 296 slope of Zn sorption isotherms for all biochars, especially for RB600, at all pH and ionic strength levels. This implies a
 297 high affinity for RB600 to adsorb Zn. Among the four studied biochars, RB600 showed the highest pH can increase the
 298 negative surface charge through the deprotonation of hydroxyl and carboxyl groups would lead to increase Zn sorption.
 299 On the other hand, earth alkaline metals (Ca and Mg) originated from R-O-M and R-COO-M surface functional groups
 300 in RB600 enter cation exchange reaction thereby raising biochar's Zn sorption capacity (Zhao et al., 2020). With
 301 increasing the ionic strength of solution, Zn adsorption by four biochars decreased at all pH levels and the lowest Zn
 302 sorption amount was for WB300.

Figure 6. Zn sorption isotherm data for WB300, WB600, RB300 and RB600 in (a) Unadjusted pH, (b) pH adjusted to 4 and (c) pH adjusted to 6

In this study, Freundlich, Langmuir and Dubinin-Radushkevich models were applied to simulate Zn sorption on the studied biochars with a good fit. The parameters r^2 , and SEE of these models are presented in Tables 5-8. Results indicated that the Freundlich and Dubinin-Radushkevich models are slightly better than Langmuir model for BW300, BW600 and BR300 with regard to r^2 and SEE values. The reason for the better fit of Freundlich model, aside from the empirical nature, can be the involvement of various mechanisms in the process of multi-layered, heterogeneous and surface adsorption. Better fitting of Freundlich model to the adsorption data in biochars derived from Scots pine wood and silver birch wood (derived at 450 and 750 °C) (Mubarak et al, 2013) and biochars derived from sugar cane bagasse, eucalyptus forest residues, and castrol meal have been reported in the literature (Doumer et al., 2016).

As with RB600, Langmuir model provided a better fit than the other two isotherms indicating that Zn sorption on this biochar probably occurred in the absence of significant interaction among the adsorbed molecules or adsorbing sites with almost equal energy (Park et al., 2016). Some scholars believed that a better fitting of Langmuir's model suggests the presence of chemisorption process (Kizito et al., 2015). Jiang et al. (2016) stated that the biochars produced at high pyrolysis temperatures (>500 °C) have a high degree of carbon crystallites because turbostatic crystallites develop, which may explain why Langmuir provides a better fit for these biochars. Studies report that heavy metal adsorption by biochar often occurs through ionic exchange and surface complexation between biochar functional groups and metal ions (Oliveira et al., 2017). Cation π bond plays a crucial role in heavy metal sorption by biochars prepared at high pyrolysis temperatures, which is in turn attributable to graphitic structures.

Results in Tables 5-8 show that high pyrolysis temperatures correlated with a rise in K_F as an adsorption capacity index. Maximum and minimum K_F values were observed in RB600 and WB300, respectively. The highest adsorption intensity was observed at pH adjusted to 6. Also, when the ionic strength of the solution increased, Zn adsorption intensity decreased. In the studied biochars, n values in Freundlich model were larger than 1, which suggests different energy levels of the Zn adsorbing surfaces.

Table 5. Freundlich, Langmuir and Dubinin-radushkevich isotherm constants for the adsorption of Zn on WB300 at different pH and ionic strength values.

pH	I.S	q_{exp200}	Langmuir			Freundlich			Dubinin-Radushkevich			
			$K_L(.10^{-2})$	q_m	r^2	K_F	n	r^2	$K_D(.10^{-3})$	q_m'	E	r^2
N.A	0.01	4.3	1.2	5.87	0.96	0.23	1.83	0.99	6.1	15.04	9.05	0.98
	0.03	3.5	0.9	5.54	0.96	0.17	1.74	0.99	6.3	13.08	8.91	0.98
	0.1	2.9	0.4	5.47	0.96	0.06	1.38	0.99	8.1	13.02	7.85	0.99
4	0.01	6.2	1.5	8.87	0.99	0.44	1.88	0.96	6.2	25.04	8.98	0.98
	0.03	5.1	0.7	8.54	0.99	0.17	1.53	0.97	8.3	25.50	7.76	0.98
	0.1	3.9	0.5	7.66	0.99	0.08	1.37	0.98	8.2	23.55	7.81	0.99
6	0.01	4.9	9.2	4.59	0.95	1.05	3.31	0.97	3.4	9.81	12.13	0.98
	0.03	4.2	7.4	4.25	0.93	0.81	3.02	0.98	3.5	9.30	11.95	0.98
	0.1	3.8	5.1	3.93	0.92	0.67	2.88	0.98	3.7	8.63	11.62	0.97

I.S: ionic strength, N.A: unadjusted pH, q_{exp200} : the maximum experimental amount of adsorbed Zn at equilibrium concentration ($mg\ g^{-1}$) q_m and q_m' : maximum adsorption capacity ($mg\ g^{-1}$), K_D : constant related to the adsorption energy ($mol^2\ kJ^{-2}$), E: sorption energy ($kJ\ mol^{-1}$).

Table 6. Freundlich, Langmuir and Dubinin-radushkevich isotherm constants for the adsorption of Zn on WB600 at different pH and ionic strength values.

pH	I.S	q_{exp200}	Langmuir			Freundlich			Dubinin-Radushkevich			
			$K_L(.10^{-2})$	q_m	r^2	K_F	n	r^2	$K_D(.10^{-3})$	q_m'	E	r^2
N.A	0.01	18.27	5.9	19.04	0.94	2.99	2.61	0.99	3.8	45.58	11.47	0.99
	0.03	16.03	3.6	18.17	0.95	2.01	2.34	0.99	4.4	44.47	10.66	0.99
	0.1	13.58	2.2	17.38	0.98	1.23	2.03	0.99	5.4	45.78	9.62	0.99
4	0.01	16.74	10.3	17.26	0.98	3.79	3.08	0.97	3.2	38.19	12.46	0.99
	0.03	15.87	7.7	16.88	0.97	2.93	2.76	0.98	3.6	37.16	11.70	0.99
	0.1	14.70	6.2	14.79	0.95	2.40	2.67	0.98	3.8	35.51	11.47	0.99
6	0.01	19.29	8.5	19.17	0.93	4.25	3.12	0.99	3.1	40.35	12.70	0.99
	0.03	17.29	7.3	18.10	0.95	3.85	3.13	0.99	3.1	37.12	12.70	0.99
	0.1	15.62	8.1	15.79	0.95	3.53	3.21	0.99	3.0	32.37	12.90	0.99

Table 7. Freundlich, Langmuir and Dubinin-radushkevich isotherm constants for the adsorption of Zn on RB300 at different pH and ionic strength values.

pH	I.S	q_{exp200}	Langmuir			Freundlich			Dubinin-Radushkevich			
			$K_L(.10^{-2})$	q_m	r^2	K_F	n	r^2	$K_D(.10^{-3})$	q_m'	E	r^2
N.A	0.01	19.54	3.1	25.79	0.99	1.91	1.95	0.98	5.4	78.48	9.62	0.99
	0.03	18.52	2.6	25.37	0.98	1.45	1.84	0.99	5.8	71.94	9.28	0.99
	0.1	16.48	2.2	23.89	0.99	1.33	1.84	0.97	5.9	71.94	9.20	0.98
4	0.01	17.56	3.3	21.81	0.99	1.88	2.08	0.99	5.0	62.78	10.00	0.99
	0.03	16.48	2.5	21.85	0.99	1.45	1.95	0.99	5.5	63.43	9.53	0.99
	0.1	14.55	2.4	20.56	0.99	1.16	1.88	0.98	5.8	60.82	9.28	0.98
6	0.01	20.92	7.1	22.77	0.94	4.44	2.91	0.99	3.3	49.05	12.30	0.99
	0.03	19.90	6.5	22.12	0.93	3.84	3.13	0.99	3.7	50.08	11.62	0.99
	0.1	17.28	4.9	19.62	0.94	2.44	2.42	0.99	4.2	47.08	10.91	0.98

Table 8. Freundlich, Langmuir and Dubinin-radushkevich isotherm constants for the adsorption of Zn on RB600 at different pH and ionic strength values.

pH	I.S	q_{exp200}	Langmuir			Freundlich			Dubinin-Radushkevich			
			$K_L(.10^{-2})$	q_m	r^2	K_F	n	r^2	$K_D(.10^{-3})$	q_m'	E	r^2
N.A	0.01	33.80	59	35.68	0.99	11.98	3.02	0.87	2.8	102.1	13.36	0.92
	0.03	33.39	69	34.26	0.97	11.84	3.10	0.86	2.7	94.83	13.60	0.91
	0.1	32.17	46	33.25	0.93	10.13	2.93	0.86	2.9	92.86	13.13	0.89
4	0.01	34.07	87	33.54	0.97	12.29	3.14	0.88	2.6	92.21	13.86	0.93
	0.03	32.21	62	33.55	0.94	11.04	3.02	0.85	2.8	92.86	13.36	0.90
	0.1	31.75	56	32.13	0.92	10.37	3.14	0.82	2.7	84.36	13.60	0.88
6	0.01	35.86	156	35.49	0.96	16.93	3.60	0.92	2.2	91.56	15.07	0.96
	0.03	34.64	87	35.28	0.99	13.84	3.27	0.92	2.4	94.83	14.43	0.96
	0.1	32.53	88	32.80	0.99	13.05	3.58	0.91	2.3	78.48	14.71	0.95

Comparing the experimental (q_{exp200}) and Langmuir adsorption maxima (q_m) in WB300 indicated that “ q_{exp200} ” at three ionic strengths used, unadjusted pH and adjusted pH 4 were lower than Langmuir “ q_m ”; however, their values were almost equal for adjusted pH at 6 (Table 5). In the case of WB600 and RB600 the Langmuir “ q_m ” value at unadjusted and adjusted pH 4 were larger than “ q_{exp200} ”, but did not differ much at pH 6 (Table 6 and 7). In RB300, “ q_m ” exceeded “ q_{exp200} ” at all pH and ionic strength values (Table 8). Close proximity of “ q_{exp200} ” and Langmuir “ q_m ” in studied biochars suggests that the monolayer completely filled with adsorbed Zn ions. While, the lower values of “ q_{exp200} ” than Langmuir “ q_m ” indicates that the adsorption monolayer is not filled yet. Jiang et al., (2016) reported a higher “ q_m ” in hard (jarrah) wood biochar (2.33 mg g⁻¹) than soft (pine) wood biochar (1 mg g⁻¹) regarding Zn sorption. Comparing Langmuir sorption affinity (K_L) in biochars demonstrated that RB600 contained highest K_L , while lowest occurred in WB300. The other two biochars were almost the same regarding this parameter. Such a difference is undoubtedly associated with dissimilar physicochemical properties of the biochars (Table 2). In rice biochars, pH, CEC and pH_{pzc} were more than in woody biochars. Moreover, compared to the latter, they contained more oxygen-containing functional groups. This is the reason for higher Zn adsorption capacity of rice biochars (Li et al., 2017). Such an effect was also evident in FTIR results (Figure 3). Another factor is higher P and N concentrations in these biochars than woody biochars (Table 2), because of high complexation constants (pK) of heavy metals with groups containing P and N (Bogusz, et al., 2019). High Si concentration, too, has a part to play in increasing adsorption capacity (Figure 2, 3).

Dubinin-Radushkevich model assumes an association between the sorption and filling the micropore volumes and seems to be better than Langmuir model in that it doesn't consider adsorption exclusively depending on a homogeneous surface with a constant adsorption potential. The highest K_D value was observed in WB300 (Table 5) in which K_D in adjusted pH 4 was more than in any other states which is well-supported by WB300's sigmoid curve (Figure 6). As the K_D dropped, the isotherms curves lost their sigmoidal shapes. Table 8 shows that the lowest K_D in RB600 is evident and H-shaped isotherms in this type support the high sorption affinity in RB600 (Hu and Zhang, 2019). Mean free energy (E) was lower than 8 only in WB300 indicating physical adsorption. Other biochars with $E > 8$ showed that Zn could be adsorbed chemically.

Physical adsorption depends on the surface characteristics such as pore structure, and according to Zhang et al. (2020) is not a significant mechanism in the case of heavy metals sorption.

3.3.1. Effects of Initial pH and ionic Strength

Initial pH of the solution is one of the most vital parameters in heavy metal sorption process since by influencing the quantity of surface charge and metal precipitation in the solution, a lot of variation in adsorption capacity and metal removal efficiency would result. Figure 7 clearly illustrates that the highest amount of Zn removal from solution occurred at pH 6 in WB600, RB300, and RB600. However, in WB300 the highest percentage of removal was observed at pH 4.

381 The more acidity of the solution, the more H^+ ion competition with Zn ions is expected to occur which keeps them away
382 from adsorbing sites.
383 In order to examine the effect of Zn sorption on solution pH, equilibrium pH (at post-adsorption stage) in all studied
384 biochars with four initial concentrations (C_i) (5, 40, 100, 200 $mg\ L^{-1}$) was measured. Results indicated that in the initial
385 pH adjusted at 4, the solution pH values rose in all biochars following Zn sorption but in adjusted pH at 6, the trend of
386 pH changes were not similar for all biochars. In the case of WB300 in all initial concentrations, pH dropped below 6 after
387 Zn sorption. While in RB600 after Zn sorption was complete, pH exceeded 6. In WB600 and RB300 in low initial
388 concentrations pH increased, but a decrease in pH after Zn sorption was observed in high initial concentrations. In Figure
389 7, Zn removal efficiency in all pH values and ionic strengths investigated in $C_i = 200\ mg\ L^{-1}$ are presented. As it is shown
390 in the Figure, except for WB300 that offers the highest efficiency for Zn removal at adjusted pH 4, the other three biochars
391 demonstrated the same efficiency at pH 6.

392

393 **Figure 7.** Zn removal in studied biochars at highest initial concentration (200 $mg\ L^{-1}$)
394

395 In rice based biochars, compared to woody biochars, higher O and oxygen-containing groups were found and O/C ratio
396 in rice biochars was higher (Table 2). Oxygen-containing groups play a crucial role in sorption of metal ions are more
397 prone to complexation with metals (Li et al., 2017). Another effective factor in different quantities of heavy metal sorption
398 by biochars is different concentration of sulfur (S), phosphorus (P), and nitrogen (N) they contain. The N concentration
399 in rice based biochars were similar to woody biochars but P concentration in WB600, WB300, RB600 and RB300
400 corresponded with the adsorption order for Zn in these biochars, which accounts for Zn complexation with P-containing
401 group. FTIR spectra confirm the presence of S groups in all derived biochars. Decrease in peak intensities following Zn
402 sorption can be justified by Zn complexation with S-containing groups. Additionally, the presence of silicon (Si) in rice
403 biochars can mean that biochars have a higher adsorption capacity (Figure 3) (Bogusz et al., 2019).
404 In this study, the highest Zn removal efficiency for all of the studied biochars and pH levels was observed at 0.01 M ionic
405 strength, while the lowest was recorded at 0.1 M ionic strength (Figure 7). As the ionic strength increased, solution K^+
406 concentration increased such that these ions were accumulated in the vicinity of biochar surface. The close correspondence
407 between K^+ ions and the surfaces can decrease interactions between Zn ions and active sites and led to reduction in Zn
408 removal. Moreover, boosted ionic strengths tend to motivate K and Zn ionic competition; therefore, K ions are deposited
409 on active adsorption sites. In this way, Zn adsorption capacity and removal efficiency of Zn diminishes (Salmani et al.,
410 2013). Wang et al. (2015) reported that with increasing solution ionic strength from 0.01 M to 0.1 M, the removal rate of
411 Cu, Cd, and Pb in pristine and engineered wood biochars decreased.

412

3.4. Desorption isotherms

Desorption experiments were performed at all three ionic strengths (0.01, 0.03 and 0.1 M).

Figure 8. Zn desorption isotherms for studied biochars, WB300 (a), WB600 (b), RB300 (c), RB600 (d)

In this study, the maximum desorption was observed in WB300; however, RB600 was found to possess a good capability for adsorption and retention of Zn. After five steps of desorption, on average of 57.0, 16.1, 35.6 and 9.5 percentage of adsorbed Zn were desorbed in solution in WB300, WB600, RB300 and RB600, respectively.

According to Figure 8, the amount of desorbed Zn from WB300, RB300 and RB600 at 0.1 M ionic strength was higher than that in the two other ionic strengths. Zn desorption showed no change at 0.01 and 0.03 M ionic strengths (Figure 8). Since in the present research, Zn desorption experiments occurred at natural pH levels, it is estimated that low desorption may have been due to pH differences in RB600 compared to WB300 (that is pH 9.6 compared to pH 5.3, respectively) (Bogusz et al., 2015). On the other hand, Zn sorption on WB300 may have occurred on external surfaces and macropores and bar the possibility of diffusion to micropores and internal surfaces which may be yet another reason for easy Zn desorption in this biochar.

Figure 9. Zinc desorption efficiency of studied biochars in five steps of desorption

Figure 9 indicates that Zn desorption efficiency in biochars were higher at the first steps of experiments. Comparing biochars demonstrated that adsorbed Zn on RB600 were more stable than in others and contains a higher amount of adsorbed Zn despite the fact that Zn desorption doesn't seem to occur smoothly. On the contrary, it is more probable to restore adsorbed Zn in WB300. Adsorption process in acidic state is reversible and Zn desorption probability following adsorption is substantial. As shown in Table 2, RB300, WB300 were acidic, but in the rest they were alkaline. Results as illustrated in Figure 9 reveal that Zn desorption was the lowest in RB600 with pH 6.9, but was the highest in WB300 with a pH 5.3. Specific irreversible adsorption rate was shown to be higher in high pH values.

4. Conclusions

The biomass and feedstock type, as well as pyrolysis temperature, have a significant impact on biochar characteristics and correspondingly on Zn adsorption-desorption capacity in aqueous solutions. Key biochar properties in Zn sorption include pH, ash content, and specific surface area were increased at higher pyrolysis temperature; however, H and C content and oxygen-containing functional groups demonstrated a decrease. Kinetic experiments confirmed that Elovich and exponential models involved the best fit as far as Zn sorption is concerned. In equilibrium state, Langmuir, Freundlich and Dubinin-Radushkevich showed a good fit for Zn sorption data with the highest capacity observed in rice based biochars. Adsorption experiments in aqueous systems indicated that the biochars derived at 600 °C pyrolysis temperature possess a higher capacity for Zn sorption than biochars pyrolyzed at 300 °C, which was due to high aromaticity and high surface area. It was also observed that with increasing pyrolysis temperature and decreasing oxygen-containing functional groups, no increase in Zn sorption was detected. This may suggests that pH, aromaticity, ash content and specific surface areas are more effective than surface functional groups. The present study could come up with the highest Zn sorption for RB600 with the desorption falling to the lowest rate. Therefore, RB600 can be used as an economical and environmentally safe sorbent for removal Zn from wastewater and as an alternative for activated carbon or other water purifiers to treat Zn in wastewater. This work offers a new alternative to transform biomass waste into a promising adsorbent for Zn removal from wastewater. The results in this research are expected to provide a firm theoretical groundwork for further application of biochars in the remediation of pollution in soils and sediments.

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Masoumeh Faryadi Shahgoli, Adel Reyhanitabar ,Nosratollah Najafi and Shahin Oustan. The first draft of the manuscript was written by Masoumeh Faryadi Shahgoli and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript .

Ethics approval and consent to participate

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Availability of data and materials

If original data of this article is necessary it can be presented.

Consent for publication and Authors' contributions

All authors of this research paper have directly participated in the planning, execution, or analysis of this study, and all authors of this paper have read and approved the final version submitted.

Ethics approval

The content of this manuscript is not now under consideration for publication elsewhere. It will not be copyrighted, submitted, or published elsewhere, while acceptance by *Journal of Environmental Science and Pollution Research* is under consideration. Regarding the aims and scope of the journal, all authors and contributors of this work have agreed on submitting the report to *Journal of Environmental Science and Pollution Research*.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Figures

Figure 1

Scanning electron micrographs of WB300, WB600, RB300 and RB600.

Figure 2

EDX spectra of WB600 and RB600 after Zn sorption, at initial Zn concentration of 200 mg L⁻¹.

Figure 3

FTIR spectra of WB300, (a) WB600, (b) RB300, (c) and RB600 (d) before and after Zn sorption, at initial concentration of 200 mg L⁻¹.

Figure 4

Adsorption kinetics of Zn by different biochars used in this study.

Figure 5

Zn sorption data for the studied biochars (a) the fitting of Elovich equation, (b) the fitting of exponential model. q_t is the amount of Zn sorption (mg Zn g^{-1}) at time t .

Figure 6

Zn sorption isotherm data for WB300, WB600, RB300 and RB600 in (a) Unadjusted pH, (b) pH adjusted to 4 and (c) pH adjusted to 6

Figure 7

Zn removal in studied biochars at highest initial concentration (200 mg L⁻¹)

Figure 8

Zn desorption isotherms for studied biochars, WB300 (a), WB600 (b), RB300 (c), RB600 (d)

Figure 9

Zinc desorption efficiency of studied biochars in five steps of desorption