



Chromium desorption kinetics influenced by the rice husk and almond soft husk modified biochar in a calcareous soil

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Abstract

This study introduced modified biochar to enhance the adsorption isotherms of hexavalent chromium in a calcareous soil. Almond soft husk and rice husk biochars as precursor reagents were applied to prepare the modified biochars with abundant amino groups for heavy metal removal. For this purpose, biochars included levels zero (without biochar or control) and 4 wt% (unmodified biochar and modified biochar). Biochars were modified separately with Fe_3O_4 , NaOH, KOH, H_2SO_4 , and HNO_3 and four levels of potassium dichromate (0–150 mg/kg soil) were used. Sampling from the treated soil was carried out 5 months after the contamination of soil with chromium. All treatments (5 g) were extracted with 25 mL of a 0.01 M EDTA solutions. The suspensions were shaken for different time periods (5 to 2880 min) at 150 rpm. Concentration of Cr was analyzed in each extract by atomic absorption spectrophotometer. The results indicated that adding rice husk and almond soft husk biochars to the soil resulted in a decrease in Cr uptake at all extraction times compared to control, whereas the rice husk biochar showed a lower reduction in Cr removal than the control compared to the almond soft husk biochar. Based on the determination coefficient and standard error, the best two-constant rate equations are considered the best predictor of the chromium release kinetics trend in the studied soil.

Keywords Chromium adsorption isotherms · Biochar · Heavy metal · Environment

Introduction

Heavy metals are naturally found in the distributed form in rock formations; however, with rapid industrialization, their concentration is tremendously increasing in the environment (Muhammad et al. 2019; Ullah and Muhammad 2020; Khan et al. 2020). One of the main problems related to heavy metals is that unlike organic contaminants, they cannot be degraded or quite removed from the environment (Bharagava and Mishra 2018). Large amounts of these metals unloaded from different sources are constantly introducing into food chains and therefore seriously affecting the metabolism, resulting in

finally the death of microorganisms, herbs, and animals (Theriault and Nkongolo 2016; Fernando et al. 2016). A lot of these wastes are enriched with different heavy metals, for example, hexavalent chromium (Cr(VI)) which creates a damaging influence on environmental health. The 21st most abounding metallic element is chromium found in the environment (Sarkar et al. 2011). Chromium (Cr) is entered into the aquatic and earthy environments via discarding of indiscriminate wastes from different industries such as leather tanning, electroplating, pulp production, timber treatment, and petroleum refining (Zhitkovich 2011). Trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the two most common species of chromium that they can be found in most of the industrial superfluous materials. Cr(III) can be sorbed by soil particles and it forms precipitates with less solubility, which prevents its leaching into soil profile, and groundwater as well as its absorption by plants (Yang et al. 2007; Reale et al. 2016; Ashraf et al. 2017; Van Ginkel et al. 2011). Cr(VI) is one of the eight most toxic chemical materials to human health and it is universally identified as one of the most carcinogenic elements (Jin et al. 2016). In addition, Cr(VI) anion known as chromate is highly soluble, and weakly adsorbed by

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Table 1 Chemical and physical properties of the soil studied

Property (unit)	Value
Soil texture	Sandy loam
Organic matter (OM, %)	(0.69 ± 0.04)
Calcium carbonate equivalent (CCE, %)	(8.32 ± 0.06)
Electrical conductivity (Ec, dS/m)	(2.18 ± 0.03)
pH	(7.50 ± 0.08)
Cation exchange capacity (CEC, cmol/kg)	(8.93 ± 0.05)
N (%)	(0.03 ± 0.01)
K (mg/kg)	(433 ± 2)
P (mg/kg)	(14 ± 0.5)
Mn (mg/kg)	(1.74 ± 0.07)
Cu (mg/kg)	(0.5 ± 0.04)
Fe (mg/kg)	(1.52 ± 0.06)
Zn (mg/kg)	(0.72 ± 0.03)
Cr (mg/kg)	(Insignificant)

soil particles which allow plants to uptake it simply from the soil, and also expose it to release into the groundwater (Rajapaksha et al. 2013). Therefore, Cr(VI) is highly active in soil and water, and it has the potential to be stored and perseveres in the long term due to its non-biodegradability (Antoniadis et al. 2018; Jobby et al. 2018). In comparison with Cr(III), Cr(VI) is about 100 times toxic to living organisms, so that it enables to cause mutagenicity, teratogenicity, and carcinogenicity; accordingly, the health hazard owing to Cr is essentially attributable to Cr(VI) (Saha et al. 2011). Usually, very poisonous Cr(VI) can be reduced to less poisonous Cr(III) by applying different biowastes including dairy manure, poultry manure, and biosolids (Singh and Rattan 2014).

Biochar, a carbonaceous material, is commonly produced as a by-product of the pyrolysis of organic

biomass under limited oxygen conditions at low temperatures (Ahmad et al. 2014). In recent years, biochar soil modification has served to increase product yields via improved soil structure, modified microbial activity, and enhanced soil nutrient supply (Liu et al. 2018). The multipurpose function of biochar includes options is as follows: (i) possible carbon sequestration factor in soil; (ii) macro and micronutrient sink in soil, therefore decreasing their leaching losses; (iii) adsorbent of heavy metals in aqueous solution and soil; and (iv) soil productivity and fertility enhancer (Novak et al. 2016). Biochar features, such as great specific surface area, porous structure, the presence of efficient functional groups (containing oxygen), and high adsorption isotherms capacity, cause the unique capability for removing pollutants in soil and water (Inyang et al. 2015).

The biochar engineering is the modified or activated state of biochar (Ok et al. 2015). In order to engineer biochar, the pristine biochars are modified by chemical, biological, and physical techniques to increase their chemical, biological, and physical properties such as porosity, specific surface area, surface functional group, pH, and cation exchange capacity. In comparison to physical modification, chemical modification can change the surface chemistry of biochar, therefore resulting in an increased adsorption isotherms capacity after the modification process (Usman et al. 2016). Biochars can be activated by applying airflow or steam (Trakal et al. 2014); they can be chemically modified by utilizing acid and alkaline compounds (Regmi et al. 2012) as well as magnetic nanoparticles (Devi and Saroha 2014). The suitable choice of biochar oxidation can provide biochar with abundant carboxyl functional groups for heavy metal removal in contaminated water and soils (Uchimiya et al. 2012). Acid modification exhibited a high increase in the BET surface area of bur cucumber plant biochar, which might be owing to the increase in porosity

Table 2 Chemical and physical properties of the residues and biochar tested

Property (unit)	Almond soft husk residues	Almond soft husk biochar
pH	(4.32 ± 0.08)	(9.81 ± 0.08)
EC (dS/m)	(1.61 ± 0.05)	(3.56 ± 0.03)
N (%)	(0.57 ± 0.04)	(0.72 ± 0.05)
P (%)	(0.13 ± 0.03)	(0.15 ± 0.01)
K (%)	(0.42 ± 0.05)	(0.63 ± 0.03)
Fe (mg/kg)	(94 ± 3)	(145 ± 3)
Zn (mg/kg)	(12.53 ± 1)	(28.32 ± -0.5)
Cu (mg/kg)	(4.27 ± 0.05)	(8.15 ± 0.5)
Mn (mg/kg)	(8.87 ± 0.08)	(13.45 ± 0.5)
Cr (mg/kg)	(Insignificant)	(Insignificant)

Table 3 Chemical and physical properties of the residues and biochar tested

Property (unit)	Rice husk residues	Rice husk biochar
pH	(5.12 ± 0.08)	(8.75 ± 0.08)
EC (dS/m)	(2.15 ± 0.06)	(2.93 ± 0.03)
N (%)	(0.97 ± 0.08)	(1.72 ± 0.03)
P (%)	(0.25 ± 0.03)	(0.32 ± 0.01)
K (%)	(0.48 ± 0.02)	(1.12 ± 0.05)
Fe (mg/kg)	(136.8 ± 2)	(143.5 ± 2)
Zn (mg/kg)	(2.87 ± 0.3)	(3.75 ± 0.08)
Cu (mg/kg)	(1.85 ± 0.06)	(2.15 ± 0.06)
Mn (mg/kg)	(65.18 ± 0.5)	(93.85 ± 3)
Cr (mg/kg)	(Insignificant)	(Insignificant)

Table 4 The kinetic equation used in the experiment

Equation number	Kinetic model	Equations	Coefficients
(1)	Zero order	$q_t = q_0 - k_0 t$	k_0 , desorption rate constant (mg/kg/s)
(2)	First order	$\ln q_t = \ln q_0 - k_1 t$	k_1 , desorption rate constant (s^{-1})
(3)	Second order	$1/q_t = 1/q_0 - k_2 t$	k_2 , desorption rate constant $[(\text{mg/kg})^{-1}]$
(4)	Third order	$1/q_t^2 = 1/q_0^2 - k_3 t$	k_3 , desorption rate constant $[(\text{mg/kg}^{-2})\text{s}^{-2}]$
(5)	Parabolic diffusion	$q_t = q_0 - k_p t^{1/2}$	K_p , desorption rate constant $[(\text{mg/kg})^{0.5}]$
(6)	Elovich	$q_t = 1/\beta \ln(\alpha_s \beta_s) + (1/\beta_s) \ln t$	α_s , (mg/kg/s), β_s $[(\text{mg/kg})^{-1}]$, Equations constants
(7)	Two-constant rate equations	$q_t = at^b$	a, (mg/kg/s), b $[(\text{mg/kg})^{-1}]$, Equations constants

q_0 : The amount of element desorbed at startup. q_t : The amount of element desorbed at time t (s)

(Vithanage et al. 2015). The oxidation with nitric acid and sulfuric acid can remarkably increase the extent of surface acidic groups on the biochar and improve its surface hydrophilicity, decrease the pH value, and create the collapse in the biochar structure and the reduction of surface area, which can notably influence the biochar adsorption isotherms efficiency of metal ions (Vithanage et al. 2015). NaOH modification can enhance the percent of surface graphitic carbon and other

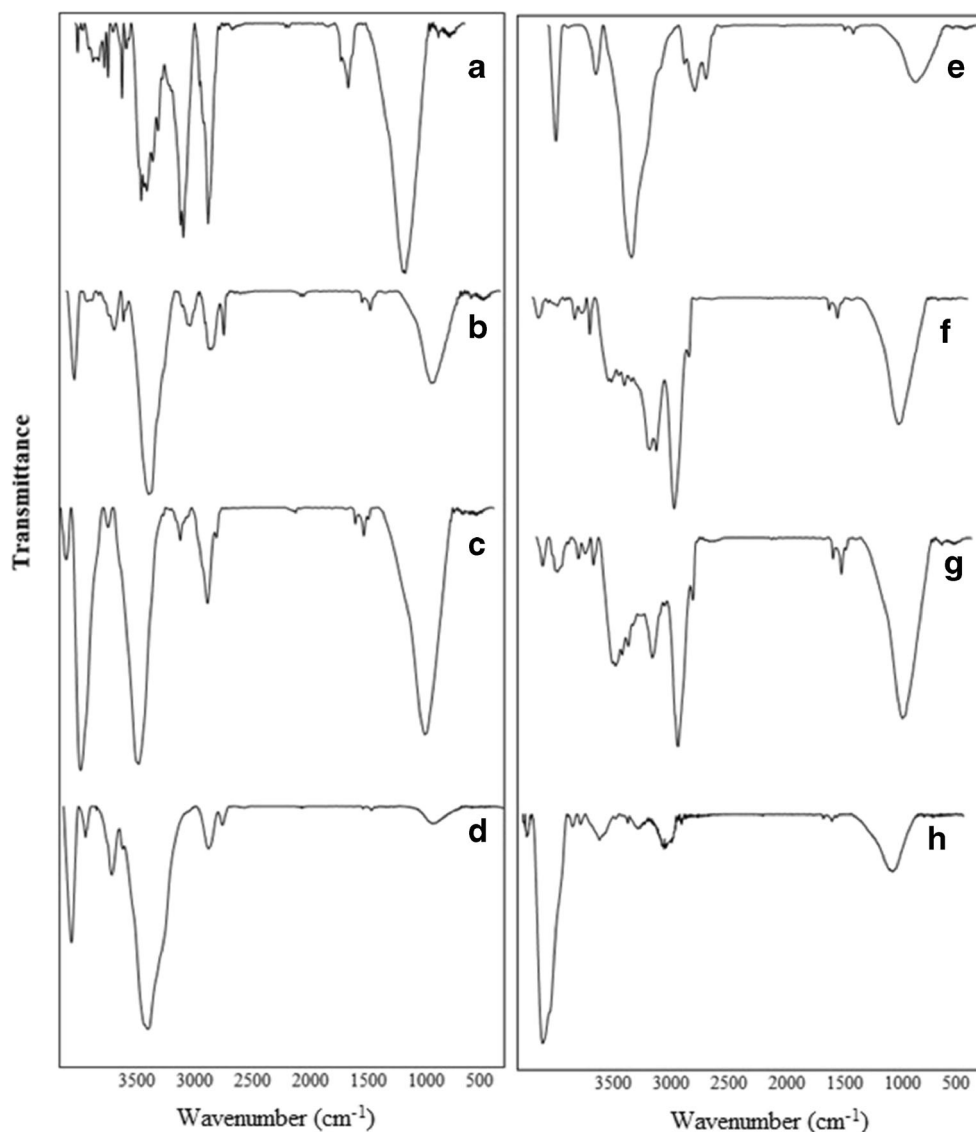
oxygen-containing compounds (Fan et al. 2010). The porous structure of biochar was adjusted by a chemical modification process using KOH (Dehkhoda et al. 2016).

Magnetic biochar composites have not only the high adsorption isotherms capacity but also the magnetic compounds under the operation of an external magnet and it is separated easily. Magnetic biochar has a broad application in purification, adsorption isotherms, and environmental

Table 5 Experimental design for incubation experiment

Treatment	Pollution with Cr	Level of rice husk biochar (RI)	Level of almond soft husk biochar (AL)
Cr ₅₀ B ₀	50 mg/kg	0 wt%	0 wt%
Cr ₅₀ B ₄	50 mg/kg	4 wt%	4 wt%
Cr ₅₀ B ₄ NaOH	50 mg/kg	4 wt%	4 wt%
Cr ₅₀ B ₄ KOH	50 mg/kg	4 wt%	4 wt%
Cr ₅₀ B ₄ magnet	50 mg/kg	4 wt%	4 wt%
Cr ₅₀ B ₄ H ₂ SO ₄	50 mg/kg	4 wt%	4 wt%
Cr ₅₀ B ₄ HNO ₃	50 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₀	100 mg/kg	0 wt%	0 wt%
Cr ₁₀₀ B ₄	100 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₄ NaOH	100 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₄ KOH	100 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₄ magnet	100 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₄ H ₂ SO ₄	100 mg/kg	4 wt%	4 wt%
Cr ₁₀₀ B ₄ HNO ₃	100 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₀	150 mg/kg	0 wt%	0 wt%
Cr ₁₅₀ B ₄	150 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₄ NaOH	150 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₄ KOH	150 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₄ magnet	150 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₄ H ₂ SO ₄	150 mg/kg	4 wt%	4 wt%
Cr ₁₅₀ B ₄ HNO ₃	150 mg/kg	4 wt%	4 wt%

Fig. 1 FTIR spectra of (a) unmodified almond soft husk biochar, (b) unmodified rice husk biochar, (c) rice husk biochar modified with Fe_3O_4 , (d) rice husk biochar modified with H_2SO_4 , (e) rice husk biochar modified with HNO_3 , (f) rice husk biochar modified with NaOH , (g) rice husk biochar modified with KOH , (h) almond soft husk biochar modified with Fe_3O_4



remediation. Generally, magnetic compounds connected with biochar are commonly iron or iron oxides, i.e., Fe (0), Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, CoFe_2O_4 , etc. (Reddy and Lee 2014).

Therefore, according to the above, the purpose of this study is to stabilize heavy metals using inexpensive methods which seems to be absolutely necessary, because rice husk and almond soft husk are available in abundance and at very low prices. At the same time, its accumulation around agricultural lands and gardens causes environmental pollution and unfavorable conditions in these areas. In this study, we investigated the effect of rice husk and almond soft husk modified biochars with Fe_3O_4 , NaOH , KOH , H_2SO_4 , and HNO_3 on the chromium desorption kinetics in contaminated calcareous soils. These modified compounds were used to remove chromium(VI) in the soil.

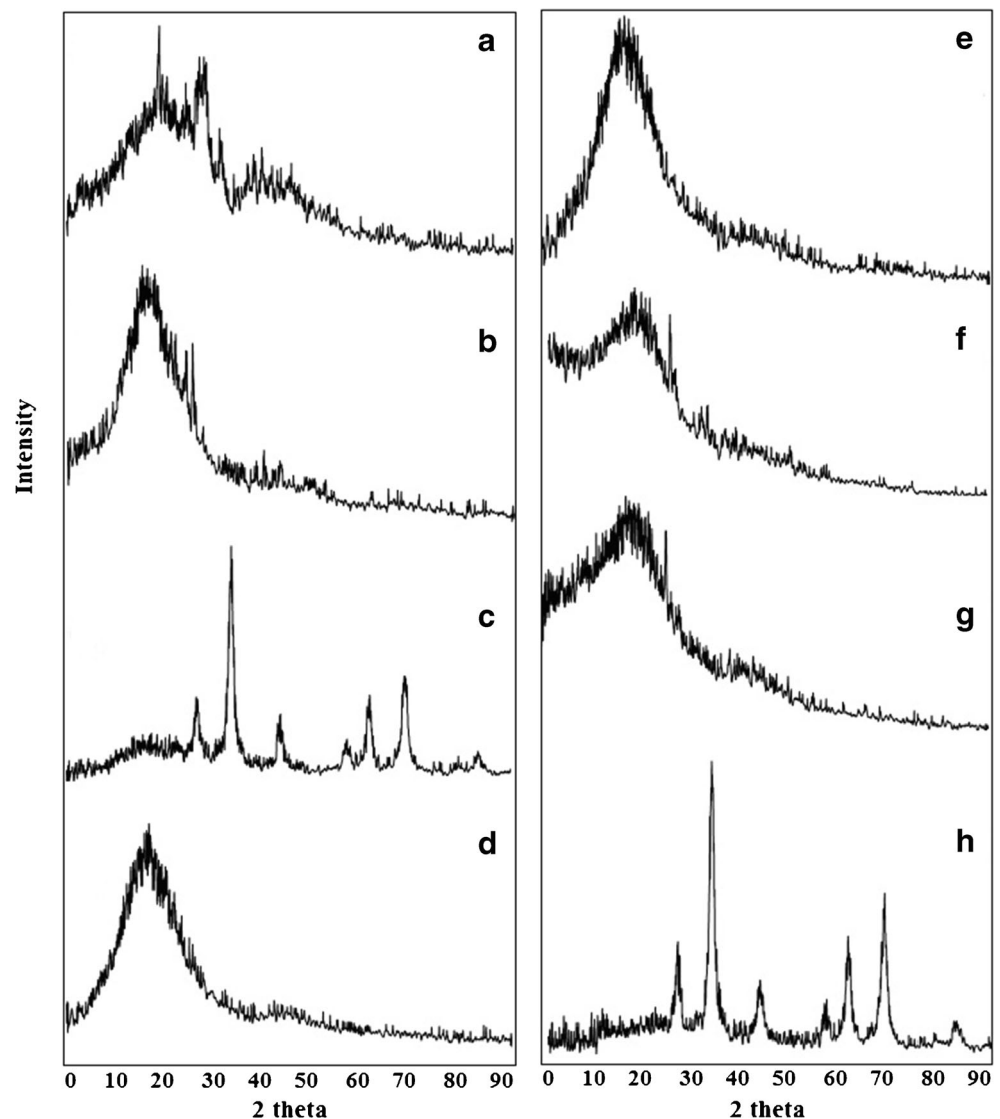
Materials and methods

Material and instruments

Sulfuric acid (H_2SO_4 , 98%), nitric acid (HNO_3 , 65%), sodium hydroxide (NaOH , 97%), potassium hydroxide (KOH , 85%), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 97%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 98%), ammonium hydroxide solution (NH_4OH , 28%), and other used materials were purchased from Sigma and Merck companies.

Fourier-transform infrared (FTIR) spectra of the compounds were performed using AVATAR spectrometer (Thermo, IET company, USA). X-ray diffraction (XRD) patterns of prepared compounds were obtained using a Philips diffractometer with monochromated high-intensity $\text{CuK}\alpha$

Fig. 2 XRD patterns of (a) unmodified almond soft husk biochar, (b) unmodified rice husk biochar, (c) rice husk biochar modified with Fe_3O_4 , (d) rice husk biochar modified with H_2SO_4 , (e) rice husk biochar modified with HNO_3 , (f) rice husk biochar modified with NaOH , (g) rice husk biochar modified with KOH , (h) almond soft husk biochar modified with Fe_3O_4 .



(Philips company, Netherlands). The field emission scanning electron microscopy (FESEM) was used to surface images of prepared materials by using the MIRA III microscope (TESCAN company, Czechia). The surface area of the prepared materials was obtained by a single-point BET method using a BELSORP MINI II (BEL company, Thailand). The samples were degassed at 150 °C for 2 h before adsorbing the N_2 gas.

Soil sampling

The soil sample was obtained from the 0–30-cm layer of a field at the Faculty of Agriculture, Kerman University, Iran. The samples were air-dried and passed via a 2-mm mesh sieve and kept in polyethylene bags prior to use. The physical and chemical properties of the selected soil were shown in Table 1. Particle size was measured by the hydrometer method

(Bouyoucos 1962); soil pH was obtained in the saturated extract of soil utilizing a combination electrode (Thomas 1996); electrical conductivity (EC) in the soil saturated extract was measured by applying a conductometer (Rhoades et al. 1996); organic matter (OM) content was obtained by dichromate oxidation (Nelson and Sommers 1996); CEC was determined by saturation with 1 M ammonium acetate (NH_4OAc) at pH = 7 (Sumner et al. 1996); calcium carbonate (CaCO_3) was measured by titration (Loeppert and Suarez 1996); accessible phosphorus (P) was determined based on the Olsen method (Olsen et al. 1954); total nitrogen was obtained by Bremner (1996) method; extractable potassium was determined by ammonium acetate molar (Chapman and Pratt 1982) and zinc (Zn), iron (Fe), manganese (Mn), and copper (Cu) concentrations were extracted by DTPA and after that determined by atomic absorption spectrophotometer (AAS) (Lindsay and Norvell 1978). Total chromium with a mixture of four acids

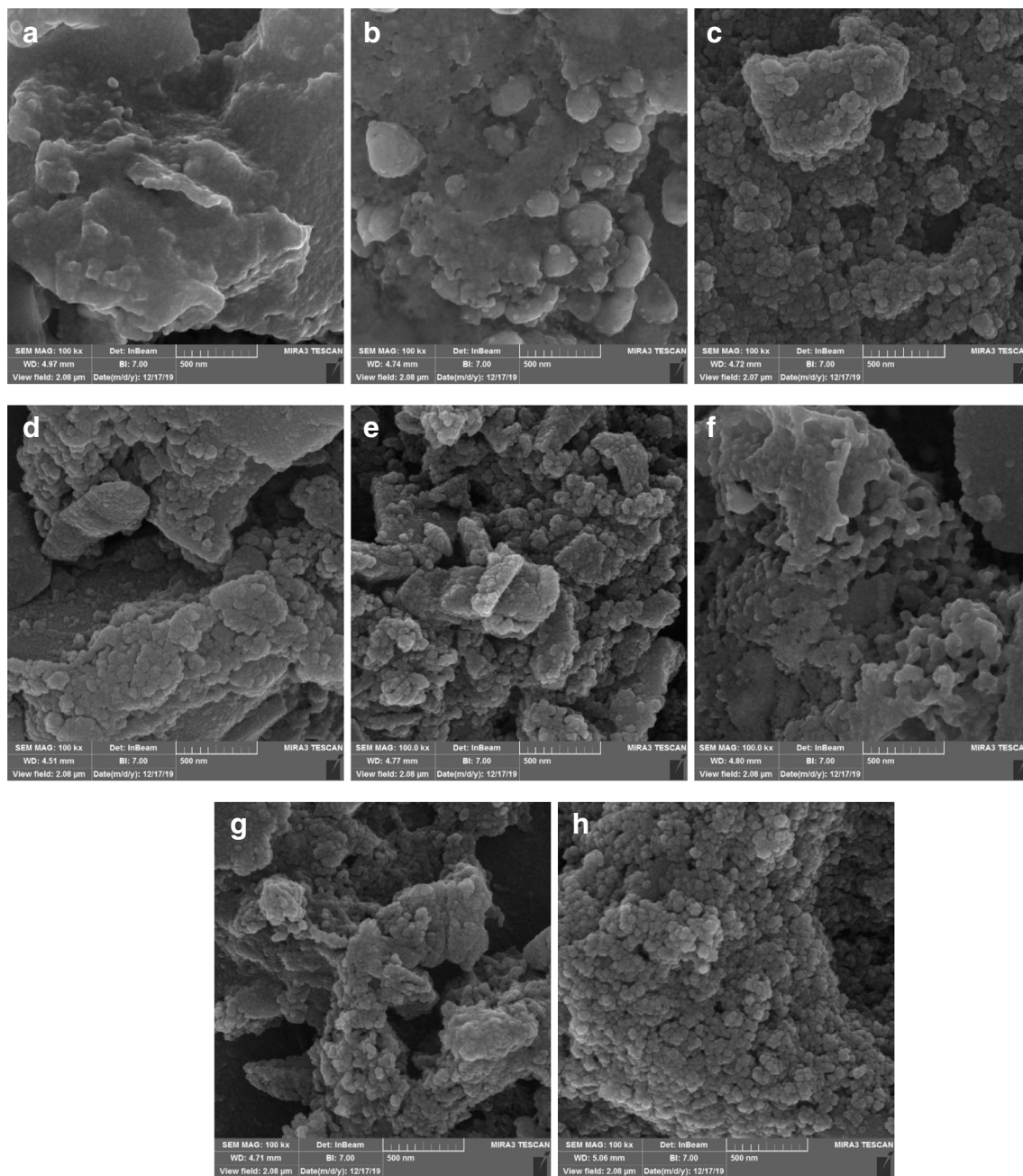


Fig. 3 FESEM images of **a** unmodified almond soft husk biochar, **b** unmodified rice husk biochar, **c** rice husk biochar modified with Fe_3O_4 , **d** rice husk biochar modified with H_2SO_4 , **e** rice husk biochar modified

with HNO_3 , **f** rice husk biochar modified with NaOH , **g** rice husk biochar modified with KOH , **h** almond soft husk biochar modified with Fe_3O_4

HF , HClO_4 , HNO_3 , and H_2SO_4 (Ma and Uren 1997) was measured and determined by atomic absorption spectrophotometer. This research was a factorial design based on a completely randomized design with four levels of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) (0, 50, 100, and 150 mg/kg soil) and biochars (almond soft husk and rice husk) included levels zero (without biochar or control) and 4 wt% (unmodified biochar and modified biochar). Biochars were modified with Fe_3O_4 , NaOH , KOH , H_2SO_4 , and HNO_3 .

Biochar production

In order to prepare the biochar and residues, the almond soft husk was prepared from the almond garden in Shiraz and rice husk was prepared from rice factory in Kamfirouz (Fars province). The residues were packed after air-drying and milling in aluminum sheets to limit the oxygenation during the pyrolysis process. Then, they were placed in the oven at $500\text{ }^\circ\text{C}$ for 4 h to produce the biochar (Hall et al. 2008). After grinding the

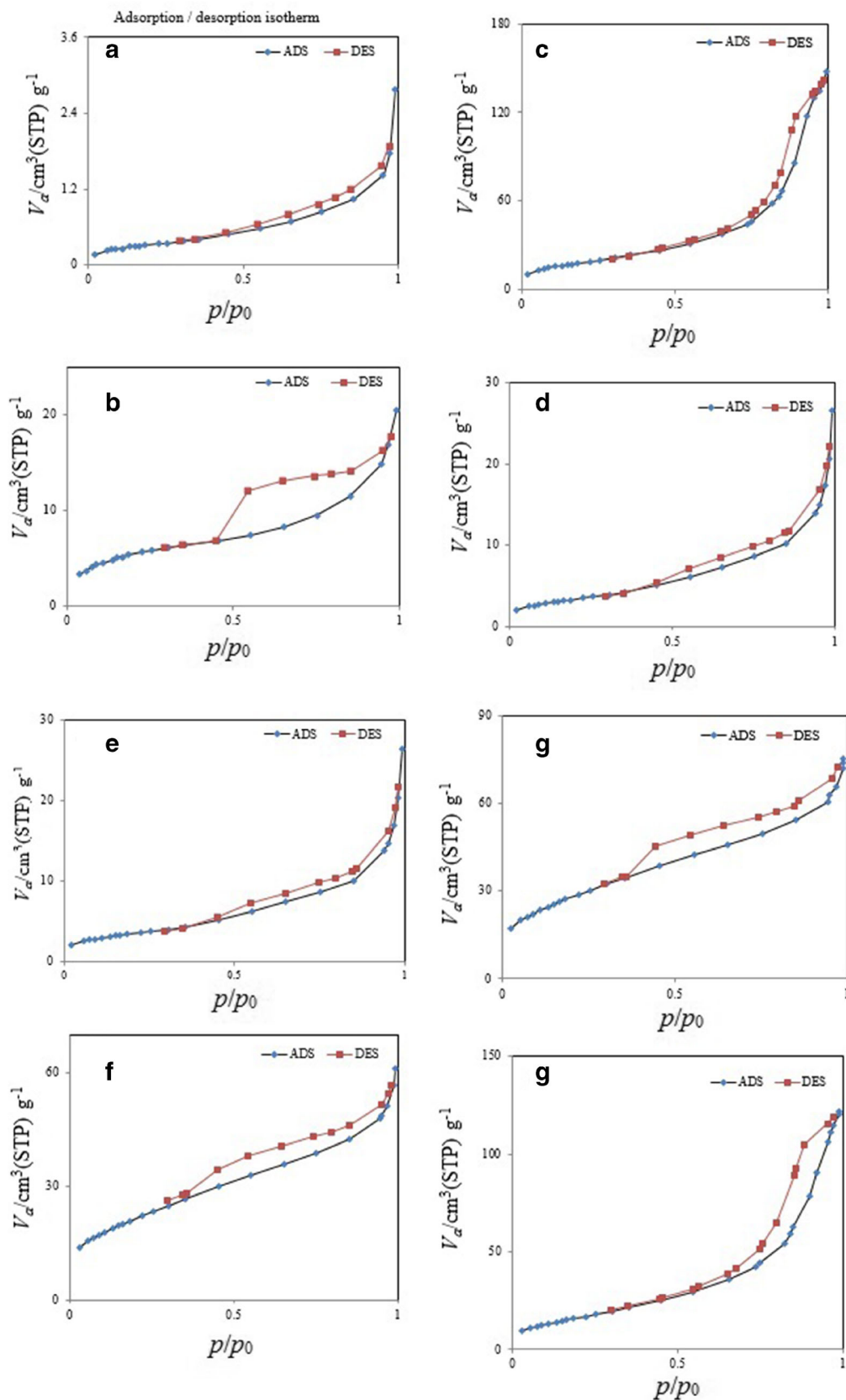


Fig. 4 Adsorption/desorption isotherms of **a** unmodified almond soft husk biochar, **b** unmodified rice husk biochar, **c** rice husk biochar modified with Fe_3O_4 , **d** rice husk biochar modified with H_2SO_4 , **e** rice

husk biochar modified with HNO_3 , **f** rice husk biochar modified with NaOH , **g** rice husk biochar modified with KOH , **h** almond soft husk biochar modified with Fe_3O_4

Table 6 Physical parameters of material by N₂ adsorption and desorption

Sample	Average diameter of the desorption pore/BJH (nm)	Volume of the desorption pore/BJH (cm ³ /g)	Area surface/BET (m ² /g)
Almond soft husk biochar	2.12	0.0042	1.192
Rice husk biochar	1.22	0.026	20.42
Rice husk biochar/Fe ₃ O ₄	2.4	0.226	67.26
Rice husk biochar/H ₂ SO ₄	2.4	0.038	12.22
Rice husk biochar/HNO ₃	2.4	0.038	12.77
Rice husk biochar/NaOH	1.22	0.099	101.17
Rice husk biochar/KOH	1.2	0.081	81.6
Almond soft husk biochar/Fe ₃ O ₄	2.4	0.191	61.03

biochars and residues (almond soft husk and rice husk) and passing through 0.5-mm sieve, some investigated chemical and physical properties were measured (Tables 2 and 3). One (1 g) of residues and biochars (almond soft husk and rice husk) was placed in an electric furnace for 4 h at 550 °C for ashing. The residues and biochars were dissolved in 2 N HCl. Then it was passed through filter paper. Zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), and chromium (Cr) concentrations were measured by atomic absorption spectrophotometer. The pH was determined in 1:5 water to residue and biochar suspension. The EC was measured in 1:5 water to residue and biochar suspension by conductivity meter, and P was obtained by Chapman and Pratt (1961), and total nitrogen by the Kjeldahl method (Bremner 1996).

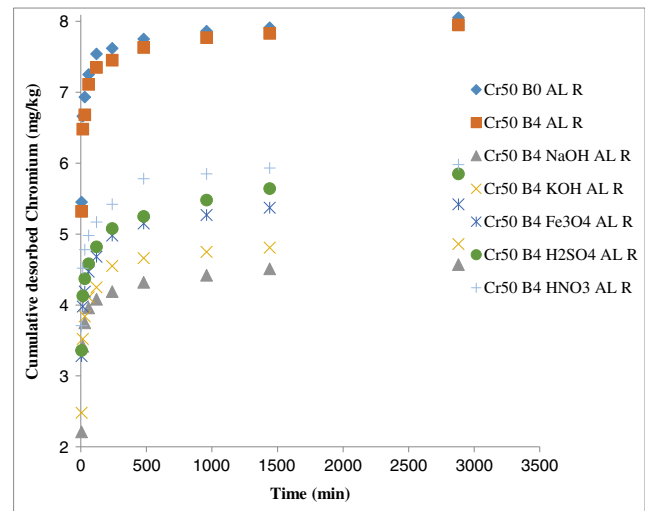


Fig. 6 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 50 mg/kg, almond soft husk biochar 5 months after incubation

Preparation the modified biochar

To modify the prepared biochars (rice husk biochar and almond soft husk biochar), 0.5 g of biochar was added to 130 mL of water and sonicated for 15 min. Then 1.5 g of FeCl₃·6H₂O and 0.5 g of FeCl₂·4H₂O were added to the above mixture and stirred for 30 min. The temperature was then brought to 60 °C, and under nitrogen atmosphere, 11 mL of NH₄OH was added to it. This mixture was stirred at 60 °C for 1 h and then separated by a magnet and washed several times with distilled water and finally dried at room temperature.

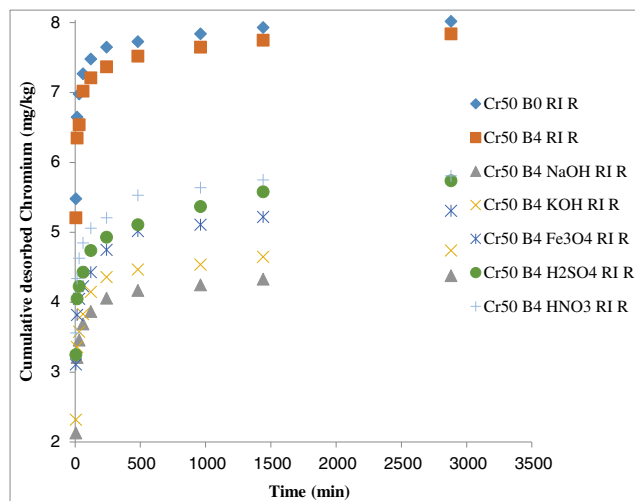


Fig. 5 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 50 mg/kg, rice husk biochar 5 months after incubation

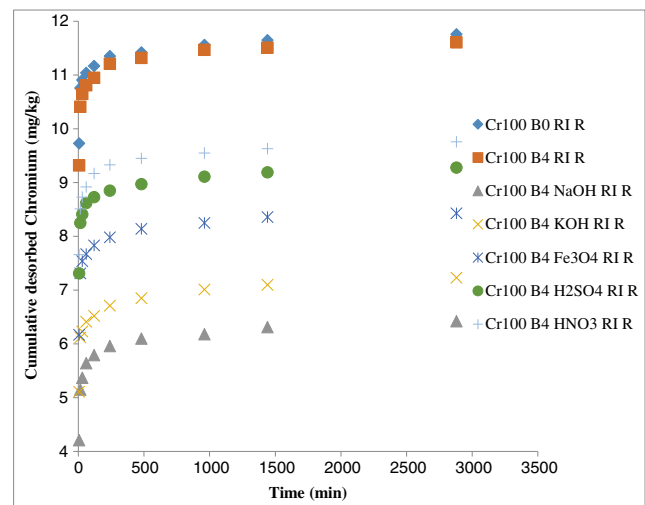


Fig. 7 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 100 mg/kg, rice husk biochar 5 months after incubation

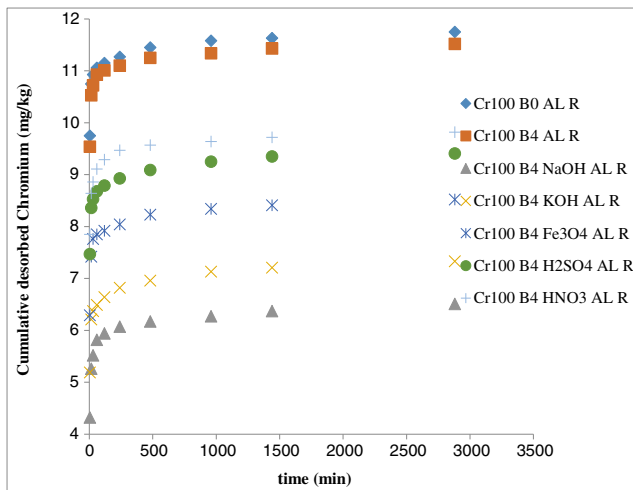


Fig. 8 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 100 mg/kg, almond soft husk biochar 5 months after incubation

To prepare biochar modified with H₂SO₄ (HNO₃, NaOH, and KOH), 1.0 g of biochar was added to 100 mL of distilled water and then 10 mL of concentrated acid (or 10.0 g of alkali) was added to it. The mixture was stirred at 60 °C for 24 h. It was finally filtered using a centrifuge and washed several times with distilled water to neutralize PH. The resulting powder was dried at 70 °C for 24 h.

Incubation assay

To perform the test, a kilogram of soil was poured into pots, then treatments almond soft husk residues, rice husk residues, and biochars were added to the soil of each pot and mixed completely. And they were placed

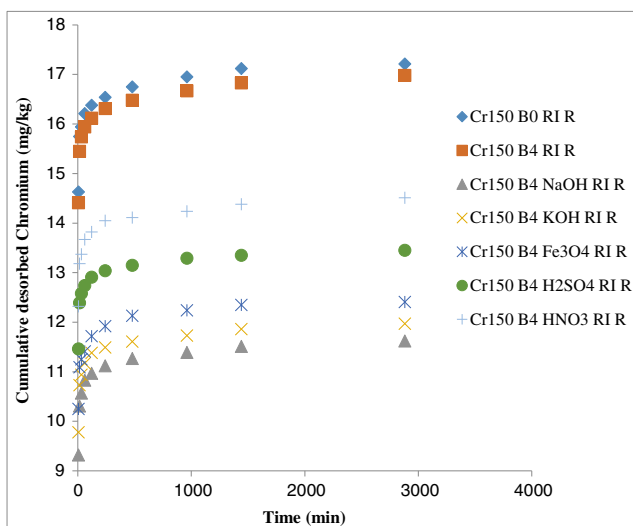


Fig. 9 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 150 mg/kg, rice husk biochar 5 months after incubation

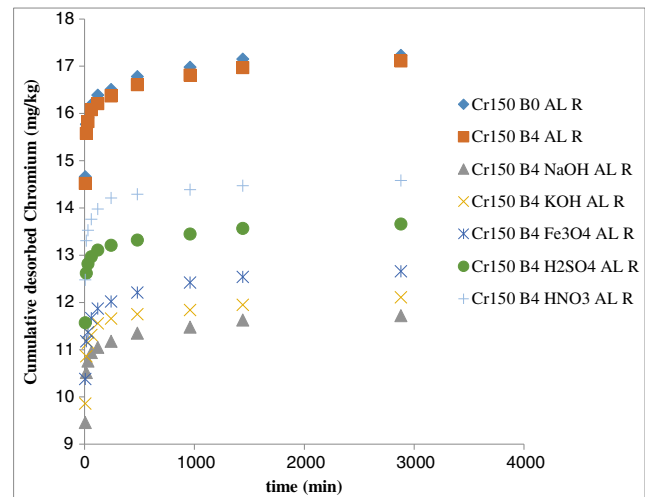


Fig. 10 Chromium desorption (cumulative) over time with the application of 0 and 4%, concentration 150 mg/kg, almond soft husk biochar 5 months after incubation

in the greenhouse under humid conditions at 25 ± 5 °C for 1 month. After 1 month of incubation, 50, 100, and 150 mg/kg of potassium dichromate was added to the soil of each pot and mixed completely. Then, they were maintained in the same conditions as before (humidity conditions at 25 ± 5 °C) for another 5 months. Soil chromium desorption kinetics was studied 5 months after incubation. The study changes in chromium desorption kinetics over a period of 5 months after incubation, all treatment soil (5 g) were extracted with 25 mL of a 0.01 M EDTA solutions. The suspensions were shaken for different time periods (5, 15, 30, 60, 120, 240, 480, 960, 1440, and 2880 min) at 150 rpm. These samples were then centrifuged at 3000 rpm for 15 min and filtered using Whatman no. 42 filter paper. Concentration of Cr was analyzed in each extract by atomic absorption spectrophotometer (Dang et al. 1994). The zero order, first order, second order, third order, Parabolic diffusion, Elovich, and two-constant equations were used to describe the kinetics of desorption of the mentioned elements. Equations that have the highest determination coefficient and the least standard error were selected as the best predictor of chromium desorption kinetics in soil. Then the coefficients of the equations with high predictive power were calculated and the mean of these coefficients was compared between different treatments (Table 4).

The standard error was obtained using the following equation:

$$SE = \left(\frac{\left(\sum (Mt - Mt^*)^2 \right)^{0.5}}{n - 2} \right) \tag{1}$$

Table 7 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of rice husk biochar, concentration 50 150 mg/kg, 5 months after incubation

Cr50 B4 HNO3 RI R	Cr50 B4 H2SO4 RI R	Cr50 B4 magnet RI R	Cr50 B4 KOH RI R	Cr50 B4 NaOH RI R	Cr50 B4 RI R	Cr50 B0 RI R		
4.71 9×10^{-6}	4.35 1×10^{-5}	4.17 9×10^{-6}	3.69 8×10^{-6}	3.48 7×10^{-6}	6.71 9×10^{-6}	6.99 8×10^{-6}	q_0 k_0	Zero order
0.46	0.57	0.51	0.33	0.34	0.38	0.34	R^2	
0.59	0.59	0.56	0.56	0.54	0.67	0.68	SE	
1.54 2×10^{-6}	1.46 2×10^{-6}	1.42 2×10^{-6}	1.29 2×10^{-6}	1.23 2×10^{-6}	1.90 1×10^{-6}	1.94 1×10^{-6}	q_0 k_1	First order
0.44	0.50	0.41	0.31	0.27	0.34	0.30	R^2	
0.12	0.13	0.13	0.19	0.20	0.11	0.10	SE	
0.22 -4×10^{-7}	0.23 -5×10^{-7}	0.24 -5×10^{-7}	0.28 -6×10^{-7}	0.30 -6×10^{-7}	0.15 -2×10^{-7}	0.14 -2×10^{-7}	q_0 k_2	Second order
0.36	0.42	0.38	0.24	0.21	0.30	0.27	R^2	
0.03	0.03	0.03	0.06	0.07	0.02	0.02	SE	
0.05 -1×10^{-7}	0.06 -2×10^{-7}	0.06 -2×10^{-7}	0.08 -3×10^{-7}	0.11 -4×10^{-7}	0.02 -6×10^{-8}	0.02 -5×10^{-8}	q_0 k_3	Third order
0.30	0.35	0.32	0.16	0.16	0.26	0.23	R^2	
0.01	0.02	0.02	0.04	0.05	0.01	0.02	SE	
4.37	3.98	3.74	3.48	3.19	6.35	6.67	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.02	0.02	k_p	
0.69	0.78	0.73	0.60	0.54	0.59	0.54	R^2	
0.42	0.38	0.39	0.51	0.49	0.56	0.56	SE	
1.98	1.41	1.44	0.96	0.89	3.69	4.18	α_s	Elovich
0.34	0.34	0.35	0.36	0.38	0.33	0.32	$s\beta$	
0.95	0.98	0.97	0.90	0.86	0.89	0.85	R^2	
0.17	0.12	0.13	0.25	0.28	0.29	0.32	SE	
0.97	0.81	0.78	0.51	0.50	1.44	1.53	a	Two-constant rate
0.11	0.11	0.11	0.11	0.11	0.06	0.05	b	equations
0.92	0.95	0.98	0.83	0.77	0.85	0.81	R^2	
0.05	0.04	0.04	0.10	0.11	0.05	0.05	SE	

where M_t is the amount of metal released (mg/kg) at time t (s), M_t^* the estimated metal value (mg/kg) of velocity equations at time t (s), and n is the number of observations (Table 5).

Results and discussion

Characterization of materials

FTIR spectra

Figure 1 showed the FTIR spectra of prepared samples. Figure 1(c, h) indicated the FTIR spectra of the magnetic nanoparticle-modified rice husk biochar and almond soft husk biochar, respectively. In fact, according to biochar peaks that appear in wavenumber 1091 cm^{-1} for C–O groups and about 2850 cm^{-1} for C–H, this indicates a higher biochar presence in the nanocomposites. But in

the spectrum (h), the dominant peak is related to Fe_3O_4 in the region of about 570 cm^{-1} , which indicates a high percentage of Fe_3O_4 than biochar. So, spectrum (c) has good magnetic properties. It can be a better adsorbent because it has higher biochar content. But it should be borne in mind that the lower the number of Fe_3O_4 nanoparticles, the lower the magnetic properties of the resulting nanocomposite will eventually be, so it cannot be a good adsorbent. Finally, experimental observations are needed for the adsorbent. The spectra of (d) and (e), which are in the acidic treatments of sulfuric acid and nitric acid respectively, show that in acidic conditions, the oxidation is higher than that in the basic treatment. According to the intensity of C–O peaks in the 1100 cm^{-1} region, it can be inferred to sodium hydroxide and potassium hydroxide, respectively, in relation to basic conditions in Fig. 1(f, g), respectively. In fact, the rate of oxidation of rice husk biochar in acidic conditions is higher than that of basic. The higher the oxidation, the

Table 8 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of almond soft husk biochar, concentration 50 mg/kg, 5 months after incubation

Cr50 B4 HNO3 AL R	Cr50 B4 H2SO4 AL R	Cr50 B4 magnet AL R	Cr50 B4 KOH AL R	Cr50 B4 NaOH AL R	Cr50 B4 AL R	Cr50 B0 AL R		
4.89 9×10^{-6}	4.47 1×10^{-5}	4.36 9×10^{-6}	3.89 8×10^{-6}	3.68 7×10^{-6}	6.82 9×10^{-6}	7.01 8×10^{-6}	q_0	Zero order
0.46	0.56	0.46	0.35	0.32	0.38	0.34	k_0	
0.57	0.54	0.55	0.64	0.62	0.68	0.68	R^2	
1.58 2×10^{-6}	1.49 2×10^{-5}	1.46 2×10^{-6}	1.34 2×10^{-6}	1.28 2×10^{-6}	1.91 1×10^{-6}	1.94 1×10^{-6}	q_0	First order
0.41	0.49	0.41	0.29	0.25	0.33	0.31	k_1	
0.12	0.13	0.13	0.18	0.20	0.11	0.10	R^2	
0.23 -3×10^{-7}	0.23 -4×10^{-7}	0.23 -4×10^{-7}	0.27 -5×10^{-7}	0.29 -5×10^{-7}	0.15 -2×10^{-7}	0.14 -2×10^{-7}	q_0	Second order
0.36	0.42	0.36	0.23	0.19	0.29	0.27	k_2	
0.03	0.03	0.03	0.06	0.07	0.02	0.02	R^2	
0.04 -1×10^{-7}	0.05 -2×10^{-7}	0.06 -2×10^{-7}	0.08 -3×10^{-7}	0.09 -3×10^{-7}	0.02 -5×10^{-8}	0.02 -5×10^{-8}	q_0	Third order
0.31	0.35	0.31	0.18	0.15	0.26	0.23	k_3	
0.01	0.02	0.02	0.03	0.05	0.01	0.01	R^2	
4.37	3.98	3.83	3.35	3.19	6.35	6.69	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.02	0.02	k_p	
0.69	0.78	0.73	0.60	0.54	0.59	0.54	R^2	
0.42	0.38	0.39	0.51	0.49	0.56	0.56	SE	
1.98	1.44	1.41	0.96	0.89	3.69	4.18	α_s	Elovich
0.35	0.35	0.35	0.36	0.37	0.34	0.33	$s\beta$	
0.95	0.98	0.97	0.90	0.91	0.89	0.85	R^2	
0.17	0.12	0.13	0.25	0.28	0.29	0.32	SE	
1.01	0.85	0.86	0.60	0.55	1.47	1.52	a	Two-constant rate
0.12	0.12	0.11	0.11	0.11	0.05	0.05	b	equations
0.92	0.95	0.93	0.81	0.72	0.84	0.81	R^2	
0.05	0.04	0.05	0.10	0.12	0.05	0.05	SE	

higher the functional groups that can adsorb the analyte sample.

XRD patterns

Figure 2 shows the X-ray diffraction patterns of the prepared samples. A comparison of the diffraction patterns of unmodified rice husk and almond soft husk biochars shows that both compounds are amorphous and disordered. The figures show that rice husk biochar is slightly more regular than almond soft husk biochar. After modifying the two biochars with Fe₃O₄ nanoparticles, the crystalline structure of the biochars improved and the peaks of the Fe₃O₄ nanoparticles appeared at angles of 30.1°, 35.6°, 43.7°, 54.2°, 57.8°, 63.5°, and 75.1°. In addition, rice husk biochar was also modified with two acids (HNO₃ and H₂SO₄) and two bases (NaOH and

KOH). The results show that acid modification does not cause much change in the amorphous structure of biochar. But the amorphous structures of biochar modified with two bases are changed and the extra peak places in these modified patterns.

FESEM Images

The FESEM images are shown in Fig. 3. As can be seen from the figures, the unmodified rice husk and almond soft husk biochars have an almost porous structure and the biochars are amorphous in accordance with their XRD patterns. By modifying biochars with Fe₃O₄ nanoparticles, the nanoscale Fe₃O₄ particles on the biochar are distributed almost spherically and uniformly.

Figures of biochar of rice modified with two acids and two bases show that both have increased the

Table 9 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of rice husk biochar, concentration 100 mg/kg, 5 months after incubation

Cr100 B4 HNO3 RI R	Cr100 B4 H2SO4 RI R	Cr100 B4 magnet RI R	Cr100 B4 KOH RI R	Cr100 B4 NaOH RI R	Cr100 B4 RI R	Cr100 B0 RI R		
8.79 7×10^{-6}	8.42 7×10^{-6}	7.49 7×10^{-6}	6.25 7×10^{-6}	5.42 8×10^{-6}	10.64 8×10^{-6}	10.88 7×10^{-6}	q_0 k_0	Zero order
0.42	0.43	0.38	0.45	0.41	0.38	0.40	R^2	
0.51	0.48	0.56	0.49	0.54	0.57	0.48	SE	
2.17 8×10^{-7}	2.13 8×10^{-7}	2.01 1×10^{-6}	1.83 1×10^{-6}	1.68 1×10^{-6}	2.36 7×10^{-7}	2.39 6×10^{-7}	q_0 k_1	First order
0.40	0.37	0.34	0.40	0.36	0.36	0.38	R^2	
0.06	0.06	0.08	0.08	0.11	0.06	0.05	SE	
0.011 -9×10^{-8}	0.11 -9×10^{-8}	0.013 -1×10^{-7}	0.16 -2×10^{-7}	0.19 -2×10^{-7}	0.09 -7×10^{-8}	0.09 -6×10^{-8}	q_0 k_2	Second order
0.37	0.34	0.30	0.36	0.32	0.33	0.35	R^2	
0.01	0.01	0.01	0.01	0.02	0.01	0.02	SE	
0.01 -2×10^{-8}	0.01 -2×10^{-8}	0.02 -3×10^{-8}	0.03 -6×10^{-8}	0.04 -9×10^{-8}	0.01 -1×10^{-8}	0.01 -1×10^{-8}	q_0 k_3	Third order
0.34	0.32	0.27	0.31	0.27	0.31	0.33	R^2	
0.01	0.01	0.01	0.01	0.01	0.02	0.02	SE	
8.50	8.17	7.21	5.97	5.13	10.34	10.63	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.01	0.02	k_p	
0.63	0.60	0.57	0.65	0.62	0.59	0.59	R^2	
0.41	0.39	0.46	0.39	0.44	0.47	0.40	SE	
6.39	6.28	5.05	3.95	2.95	8.11	8.73	α_s	Elovich
0.29	0.29	0.31	0.32	0.35	0.31	0.26	$s\beta$	
0.92	0.88	0.86	0.91	0.91	0.88	0.86	R^2	
0.20	0.21	0.27	0.21	0.22	0.25	0.23	SE	
1.93	1.90	1.71	1.42	1.22	2.12	2.19	a	Two-constant rate
0.03	0.03	0.11	0.05	0.11	0.03	0.02	b	equations
0.83	0.83	0.84	0.87	0.86	0.85	0.84	R^2	
0.03	0.03	0.04	0.04	0.05	0.03	0.02	SE	

number of cavities in biochar and this increase is more in biochars modified with alkali compounds, especially KOH.

Therefore, it can be concluded that the amount of cavities created in rice husk biochar is higher in the presence of potassium hydroxide alkaline composition and may indicate that this modified biochar structure can remove the desired contaminants than acid-modified biochars.

N₂ adsorption isotherms and desorption studies

The adsorption isotherms and desorption isotherms for nitrogen for the prepared samples are shown in Fig. 4. The surface area of unmodified almonds soft husk and rice husk was 1.92 and 20.42 m²/g, respectively. After modification of these biochars with Fe₃O₄ nanoparticles, the surface area of both biochars has increased dramatically, so it can be said that by modifying the biochar

surface with Fe₃O₄ nanoparticles, it can be theoretically stated that the ability to adsorb pollutants increases.

On the other hand, biochar modification of rice husk with nitric acid and sulfuric acid reduced the surface area compared to unmodified biochar but its pore diameter almost doubled. In addition, biochar modification of rice husk with sodium hydroxide and potassium hydroxide showed that the surface area increased very dramatically, reaching from 20.42 to 101.17 and 81.6 m²/g for KOH and NaOH, respectively, which is consistent with FESEM images (Table 6). Here, the diameter of the pores has not changed, but the volume of the pores has almost five times.

Desorption kinetics of chromium in soil

Figures 5, 6, 7, 8, 9, and 10 show the effect of adding almond soft husk and rice husk biochar to the soil on Cr uptake at different extraction times compared to

Table 10 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of almond soft husk biochar, concentration 100 mg/kg, 5 months after incubation

Cr100 B4 HNO3 AL R	Cr100 B4 H2SO4 AL R	Cr100 B4 magnet AL R	Cr100 B4 KOH AL R	Cr100 B4 NaOH AL R	Cr100 B4 AL R	Cr100 B0 AL R		
8.94 7×10^{-6}	8.53 7×10^{-6}	7.62 7×10^{-6}	6.35 8×10^{-6}	5.55 7×10^{-6}	10.70 6×10^{-6}	10.88 7×10^{-6}	q_0 k_0	Zero order
0.41	0.44	0.36	0.44	0.39	0.37	0.41	R^2	
0.50	0.46	0.55	0.50	0.54	0.49	0.48	SE	
2.19 8×10^{-7}	2.14 8×10^{-7}	2.03 9×10^{-7}	1.85 1×10^{-6}	1.71 1×10^{-6}	2.39 6×10^{-7}	2.39 6×10^{-7}	q_0 k_1	First order
0.37	0.41	0.32	0.39	0.35	0.35	0.38	R^2	
0.06	0.06	0.08	0.08	0.10	0.05	0.05	SE	
0.11 -8×10^{-8}	0.12 -9×10^{-8}	0.13 -1×10^{-7}	0.16 -2×10^{-7}	0.18 -2×10^{-7}	0.09 -5×10^{-8}	0.09 -5×10^{-8}	q_0 k_2	Second order
0.35	0.38	0.29	0.35	0.30	0.33	0.36	R^2	
0.01	0.01	0.01	0.01	0.02	0.02	0.02	SE	
0.01 -2×10^{-8}	0.01 -2×10^{-8}	0.02 -3×10^{-8}	0.03 -5×10^{-8}	0.03 -8×10^{-8}	0.01 -1×10^{-8}	0.01 -1×10^{-8}	q_0 k_3	Third order
0.33	0.35	0.26	0.31	0.26	0.30	0.33	R^2	
0.01	0.01	0.01	0.01	0.02	0.02	0.02	SE	
8.50	8.16	7.20	5.97	5.13	10.34	10.63	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.02	0.02	k_p	
0.63	0.60	0.57	0.65	0.63	0.59	0.59	R^2	
0.41	0.39	0.46	0.39	0.44	0.47	0.40	SE	
6.39	6.28	5.05	3.95	2.95	8.11	8.73	α_s	Elovich
0.29	0.29	0.30	0.30	0.32	0.28	0.26	β_s	
0.92	0.88	0.86	0.90	0.90	0.88	0.86	R^2	
0.20	0.21	0.27	0.21	0.22	0.25	0.23	SE	
1.93	1.89	1.72	1.48	1.26	2.17	2.19	a	Two-constant rate
0.03	0.03	0.04	0.04	0.01	0.02	0.02	b	equations
0.89	0.88	0.79	0.86	0.83	0.83	0.85	R^2	
0.02	0.02	0.04	0.04	0.05	0.02	0.02	SE	

control. Changes caused by several time periods (5, 15, 30, 60, 120, 240, 480, 960, 1440, and 2880 min) on chromium desorption in the treated soil are 150 days after incubation.

In all figures, the amount of chromium desorbed by the extractant in the studied soil increased cumulatively over time (5 to 2880 min). The rate of desorption was rapid at first and early times (first 2 h) and then with desorption time slower (8 h) and finally, equilibrium was observed in the treated and control samples. Adding rice husk and almond soft husk biochar to the soil resulted in a decrease in Cr uptake at all extraction times compared to control, whereas the rice husk biochar compared to almond soft husk biochar caused a significant decrease in the amount of Cr desorption compared to the control soil. The highest amount of chromium desorption is related to soil without biochar treatment. The highest chromium desorption was in untreated soil with rice husk and almond soft husk biochar

(control), while the lowest desorption rate of chromium in soil with rice husk and almond soft husk modified biochar with NaOH was at 4 wt%. However, rice husk biochar had a better effect than almond soft husk biochar. The results showed the application of rice husk and almond soft husk modified with NaOH in the treatment of 50 mg/kg, and chromium contamination compared to the control soil in the period of 5 months after incubation, and the amount of chromium desorption after 8 h of in soil was reduced by 46% and 44%, respectively. Also in the treatment of 100 mg/kg, the amount of chromium desorption was reduced by 46.52% and 46.11%, respectively, while this reduction in the 150 mg/kg treatment was 32.72% and 32.36%. However, the modified biochars showed more efficient Cr(VI) reduction compared to the untreated biochars because of the presence of effective oxygen-containing surface functional groups (Mandal et al. 2016). The adsorptive removals of chloramphenicol (CAP) on the

Table 11 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of rice husk biochar, concentration 150 mg/kg, 5 months after incubation

Cr150 B4 HNO3 RI R	Cr150 B4 H2SO4 RI R	Cr150 B4 magnet RI R	Cr150 B4 KOH RI R	Cr150 B4 NaOH RI R	Cr150 B4 RI R	Cr150 B0 RI R		
13.47 8×10^{-6}	12.54 7×10^{-6}	11.37 8×10^{-6}	10.98 8×10^{-6}	10.59 8×10^{-6}	15.74 9×10^{-6}	15.99 9×10^{-6}	q_0 k_0	Zero order
0.45	0.41	0.46	0.42	0.41	0.47	0.46	R^2	
0.52	0.49	0.53	0.53	0.56	0.59	0.60	SE	
2.60 6×10^{-7}	2.53 5×10^{-7}	2.42 7×10^{-7}	2.39 7×10^{-7}	2.36 7×10^{-7}	2.76 6×10^{-7}	2.77 6×10^{-7}	q_0 k_1	First order
0.43	0.38	0.44	0.39	0.38	0.45	0.44	R^2	
0.04	0.04	0.05	0.05	0.05	0.04	0.04	SE	
0.07 -4×10^{-8}	0.08 -4×10^{-8}	0.09 -6×10^{-8}	0.09 -6×10^{-8}	0.09 -7×10^{-8}	0.06 -4×10^{-8}	0.06 -4×10^{-8}	q_0 k_2	Second order
0.41	0.36	0.42	0.37	0.36	0.43	0.42	R^2	
0.01	0.01	0.01	0.01	0.01	0.02	0.02	SE	
0.01 -6×10^{-9}	0.01 -7×10^{-9}	0.01 -1×10^{-8}	0.01 -1×10^{-8}	0.01 -1×10^{-8}	0.01 -5×10^{-9}	0.01 -4×10^{-9}	q_0 k_3	Third order
0.39	0.34	0.40	0.34	0.33	0.40	0.40	R^2	
0.02	0.02	0.01	0.01	0.01	0.02	0.02	SE	
13.17	12.32	11.05	10.69	10.29	15.39	15.64	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.01	0.02	k_p	
0.65	0.60	0.68	0.62	0.61	0.68	0.67	R^2	
0.41	0.40	0.41	0.43	0.45	0.46	0.47	SE	
10.98	10.40	8.77	8.55	8.03	12.88	13.11	α_s	Elovich
0.31	0.32	0.32	0.35	0.37	0.32	0.30	$s\beta$	
0.93	0.88	0.95	0.90	0.90	0.93	0.92	R^2	
0.19	0.21	0.17	0.22	0.24	0.22	0.23	SE	
2.41	2.37	2.20	2.17	2.12	2.57	2.59	a	Two-constant rate
0.02	0.02	0.03	0.03	0.03	0.02	0.02	b	equations
0.91	0.87	0.93	0.88	0.87	0.91	0.91	R^2	
0.02	0.02	0.02	0.02	0.02	0.02	0.02	SE	

renewable bioresource of biochar (BC) and modified bamboo charcoal were investigated and compared. The adsorption isotherms of CAP on BC and H₂SO₄-modified BC was very slight, but on NaOH-modified BC was greatly increased. It was found that NaOH treatment increased the percentage of surface graphitic carbon and other oxygen-containing functional groups. The increased adsorption isotherms on BC–NaOH was ascribed to the enhanced π – π interaction between the adsorbent and adsorbate. It is proposed that NaOH-modified BC was effective for the adsorption isotherms of CAP in wastewater (Fan et al. 2010). Engineered biochar was obtained through the slow pyrolysis of hickory wood and then further modified with NaOH. After modification, biochar's surface area, cation exchange capacity, and thermal stability were significantly improved. The modified biochar exhibited much larger (2.6–5.8 times) metal adsorption isotherms capacities than the pristine biochar. Competitive batch adsorption

isotherms of mixed metal ions (Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Ni²⁺) showed preferential adsorption isotherms of Pb²⁺ and Cu²⁺ onto the modified biochar. The alkali-modified biochar in a fixed-bed column also showed a strong ability to filter heavy metals from aqueous solutions. The alkali-modified biochar thus can serve as an alternative adsorbent for heavy metals. This work showed that alkali (NaOH) modification greatly increased the surface area, oxygen-containing surface functional groups, and CEC of biochar derived from hickory wood. As a result, the modified biochar showed much higher sorption of heavy metal ions (i.e., Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Ni²⁺) than the original one in both single-metal and mixed-metal systems. In addition, a fixed-bed column packed with the modified biochar showed good filtration of heavy metal ions and preferentially removed Pb²⁺ and Cu²⁺ out of the mixed-metal solution. The spent column was flushed with a 0.2 M HCl solution, which desorbed all of the metal ions with Pb²⁺

Table 12 Fixed coefficients, coefficient of determination (R^2), and standard error of estimation (SE) of kinetic equations of chromium desorption in treated soil with of almond soft husk biochar, concentration 150 mg/kg, 5 months after incubation

Cr150 B4 HNO3 AL R	Cr150 B4 H2SO4 AL R	Cr150 B4 magnet AL R	Cr150 B4 KOH AL R	Cr150 B4 NaOH AL R	Cr150 B4 AL R	Cr150 B0 AL R		
13.62	12.78	11.50	11.13	10.72	15.85	16.01	q_0	Zero order
8×10^{-6}	7×10^{-6}	9×10^{-6}	7×10^{-6}	8×10^{-6}	1×10^{-5}	1×10^{-5}	k_0	
0.41	0.39	0.50	0.39	0.42	0.48	0.47	R^2	
0.53	0.50	0.53	0.55	0.54	0.59	0.60	SE	
2.61	2.55	2.44	2.41	2.37	2.76	2.77	q_0	First order
5×10^{-6}	5×10^{-6}	8×10^{-6}	7×10^{-6}	7×10^{-6}	6×10^{-5}	6×10^{-5}	k_1	
0.40	0.37	0.47	0.37	0.39	0.46	0.45	R^2	
0.04	0.04	0.05	0.05	0.05	0.04	0.04	SE	
0.07	0.08	0.09	0.09	0.09	0.06	0.06	q_0	Second order
-4×10^{-8}	-4×10^{-8}	-6×10^{-8}	-6×10^{-8}	-6×10^{-8}	-4×10^{-8}	-4×10^{-8}	k_2	
0.38	0.35	0.45	0.34	0.36	0.43	0.43	R^2	
0.01	0.01	0.01	0.01	0.02	0.02	0.02	SE	
0.01	0.01	0.01	0.01	0.01	0.01	0.01	q_0	Third order
-6×10^{-9}	-6×10^{-9}	-1×10^{-8}	-1×10^{-8}	-1×10^{-8}	-5×10^{-9}	-4×10^{-9}	k_3	
0.36	0.33	0.42	0.32	0.34	0.41	0.41	R^2	
0.01	0.01	0.01	0.01	0.02	0.02	0.02	SE	
13.17	12.32	11.05	10.69	10.29	15.39	15.64	q_0	Parabolic diffusion
0.01	0.01	0.01	0.01	0.01	0.01	0.02	k_p	
0.65	0.60	0.68	0.62	0.61	0.68	0.67	R^2	
0.41	0.40	0.41	0.43	0.45	0.46	0.47	SE	
10.98	10.40	8.77	8.55	8.03	12.88	13.10	α_s	Elovich
0.31	0.31	0.31	0.32	0.35	0.30	0.27	β_s	
0.93	0.88	0.94	0.90	0.87	0.93	0.92	R^2	
0.19	0.21	0.17	0.22	0.24	0.22	0.23	SE	
2.43	2.37	2.21	2.19	2.14	2.58	2.60	a	Two-constant rate equations
0.02	0.02	0.03	0.03	0.03	0.02	0.02	b	
0.91	0.83	0.95	0.85	0.86	0.92	0.92	R^2	
0.02	0.02	0.02	0.02	0.03	0.01	0.01	SE	

desorption efficiency of 100.6%. The regenerated column effectively removed Pb^{2+} from aqueous solution and most of the retained Pb^{2+} could be released by the acid solution. Findings from this work indicated that the alkali modification method can be applied to biochar to enhance its heavy metal removal ability and the resulting modified biochar has great potential as an alternative adsorbent for environmental remediation (Ding et al. 2016).

Comparison of the kinetics of chromium desorption equations

The values of the determination coefficient (R^2) and standard error of estimation (SE) were obtained by fitting the chromium desorption data to the kinetic equations for soil 5 months after incubation under the effects of treatments; the results are shown in Tables 7, 8, 9, 10, 11, and, 12. Determination of the best kinetic equations is usually according to the R^2 and SE; in other words, equations that have a high R^2 and a low SE

are selected as equations that best describe the rate of chromium desorption. The results obtained from these equations were investigated for the period of 5 months after incubation under treatments rice husk and almond soft husk modified biochar. The kinetic equations of zero, first, second, and third order due to the low the values of the determination coefficient cannot predict chromium desorption in soil samples. Fitting the chromium desorption data from the soils with the parabolic diffusion equation showed that due to the low R^2 and the relatively high SE, this equation cannot be a suitable equation for describing chromium desorption from the studied soils. Based on the values obtained from the R^2 and SE, two-constant rate equations were introduced as the best equation for chromium desorption kinetics (Tables 7–12). Although the Elovich equation has determination coefficient of determination similar to two-constant rate equations, but due to the high standard error of estimation, it could not be used as an appropriate equation for the investigation of chromium desorption kinetics. The values of the velocity constants α_s and β_s of the

Elovich equation in the soil show many variations (Tables 7–12). Increasing the value of β_s and decreasing the value of α_s indicate a decrease in chromium desorption rate; with increasing β_s , the rate of desorption decreases; α_s value is lower in soils with less desorption. The α_s constant is a useful parameter to predict the availability of elements in the soil. These results indicate that the application of higher levels of biochar in the soil reduces the availability of chromium in the soil. Also the use of modified biochar with NaOH and KOH reduced the desorption kinetics of chromium in the soil compared to the application of other modified biochars. Coefficients in the two-constant rate equations using modified biochars were reduced compared to the control, so the rate of chromium desorption in soil was also reduced. In the two-constant rate equations with the application of modified biochars, the coefficient a decreased compared to the control, which indicates a decrease in the rate of chromium desorption in the soil. The values of k_p and q_0 constants of the parabolic diffusion equation were decreased compared to the control, indicating a decrease in chromium desorption in the modified biochar samples compared to the control treatment.

Conclusion

In general, the mechanisms of adsorption isotherms of heavy metals by biochar include electrostatic interactions, ion exchange, chemical deposition, and formation of complexes with functional groups at the biochar surface. Biochar has organic functional groups on its surface (hydroxyl, carboxyl, and carbonyl), which can increase the cation exchange capacity of the soil and increase the formation of complexes with heavy metals. According to the results of this study, the amount of chromium extracted by EDTA at different times showed that the amount of desorbed chromium decreased in soils treated with biochar. The highest chromium desorption was in untreated soil with rice husk and almond soft husk biochar (control), while the lowest desorption rate of chromium in soil with modified biochar (rice husk and almond soft husk) with NaOH was at 4 wt%. However, rice husk biochar showed a greater reduction compared to almond soft husk biochar. It can be stated that rice husk biochar has been more successful than soft almond peel biochar due to its more porous structure and cation exchange capacity. Due to the above, it can be possible to recommend the use of biochar as a modifier in soils contaminated with this element. Evaluation of chromium desorption data from studied soil with different kinetic equations showed that chromium desorption data had fits good with two-constant rate equations. In this study, it can be reported that two-constant rate equations are introduced as the best descriptive equation for desorption of chromium in soil samples 5 months after incubation.

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