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Thermodynamics and removal process of heavy metals from drilled mud water. Selecting a better model of adsorption isotherm

Zohre Lajmiri Orak[a], Sima Sabzalipour[a,*], Ebrahim Panahpour[b], Sina Attar Roshan[a], Haman Tavakkoli[c]

[a]*Department of Environment, Ahvaz Branch, Islamic Azad University, Post Code: 61349-37333, Post Office: 1915, Ahvaz, Iran, Mobile: (+98) 9163121821; emails: shadi582@yahoo.com/sabzalipoursima@gmail.com (S. Sabzalipour), Z_lajmiri@yahoo.com (Z.L. Orak), sina_2934@yahoo.com (S.A. Roshan)*
[b]*Department of Soil Science, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran, email: e.panahpour@gmail.com (E. Panahpour)*
[c]*Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran, email: htavakkoli59@gmail.com (H. Tavakkoli)*

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ABSTRACT

This study aimed to investigate the thermodynamics and removal process of heavy metals from drilled mud water by using pyrolysis of *Conocarpus* wastes and to select a better model of adsorption isotherm. The biochar samples were transferred to a laboratory, air-dried, and then kept in an oven at 50°C for 2 h. In this study the experiments were performed in batch mode and initial concentration of the heavy metals, biosorbent dose pH, ionic strengths, temperature, and contact time on the biosorption process. The sequential effect extraction method was used to calculate the reduced partition index or stability index (IR) and the mobility factor (MF) after 1, 2, 4 and 8 weeks of incubation. The results showed that the removal efficiency and adsorption capacity of adsorbents decreased with increases in the initial concentration. The biosorption kinetics was controlled by the pseudo-second-order model (R^2 = 0.99–1, p-values ≤ 0.01). The results suggested that the application of *Conocarpus* biochar (CB) in drilling wastes can significantly increases the residual zinc (Zn), copper (Cu), and cadmium (Cd) but reduce the bioavailability and mobility of these metals. Based on the results, after 8 weeks of incubation, the treatment of 10% biochar significantly reduced the carbonate (3%–16%) and exchange (6%–9%) of the studied metals (p-values < 0.05). Also, the number of mobility factors for Cd, Cu, and Zn were reduced to 22%, 6%, and 19%, respectively. Moreover, it was observed that the application of *Conocarpus* biochar resulted in broader distribution of metals in stable forms and thus increased the amount of partition index, indicating a decrease in the mobility factor. Overall, the findings revealed that the addition of *Conocarpus* biochar at the highest rate (10%) as a low-cost modifier to drilled mud water leads to the deformation of Cd, Cu, and Zn from irregular forms to stable forms and reduces the mobility of these metals.

Keywords: Heavy metal; Biochar; Absorption; Thermodynamic; *Conocarpus*; Water; Drilling mud

1. Introduction

In recent decades, due to the importance of global and regional pollutants and their effects on human health, environmental pollution has captured a lot of attention [1–3]. Environmental pollution is caused by the activities of the drilling industry exploring and producing heavy metals in drilled mud water, discharging them into the soil, surface water, groundwater, and air [4–7]. Having toxicity and accumulation properties, heavy metals are hazardous for humans and the environment [8–10].

* Corresponding author.

The development of industries has increased the contamination of the environment with heavy metals [11,12]. The most common routes of emission of heavy metals in the environment are combustion, drill cutting, and chemical manufacturing [13]. In the gas and petroleum industry, toxic substances, especially heavy metals, available in drilling wastes, are one of the main volumes of waste produced, which are potentially harmful to the ecosystems [14]. The ability to move and change shape in the soil, non-biodegradability, stability, and toxicity are the important properties of heavy metals (HM) [15]. Skin allergy, decreased bodyweight, headache, low intelligence quotient (IQ), mutagenic effects, diarrhea, nervous and cardiovascular systems diseases, blood and bone diseases, genotoxicity, impaired lung function, DNA destruction, thrombosis symptoms, cardiovascular disease, and lung and stomach cancer are the most important health effects resulting from exposure to heavy metals [16,17]. Food (vegetable, milk, and meat), smoking cigarettes, drinking water, soil, wastewater, inhalation, dermal contact, and breathing exhaust fumes are the main ways through which heavy metals enter the human body [18,19]. Based on the result of several studies, adsorption, ion exchange, electrochemical precipitation, and reverse osmosis are the main chemical and physical processes that can reduce or remove heavy metals entering the environment due to industrialization and rapid urbanization [4,20].

Biosorption is a physical or chemical process in molecules in which ions are absorbed into a mass of matter from a gas, liquid, or solid, and in this process, the adsorbent mass is drawn [17,21,22]. Biosorption is one of the primary treatment methods with excellent efficiency in removing pollutants, especially heavy metals [20,23,24].

Gasification and hydrothermal carbonization and pyrolysis with a porous carbon material are the most important production methods of biochar [25]. Biochar can extensively reduce the mobility of HM and other contaminants in soil [26]. For this reason, today in soils, the use of biochar is produced from forest wastes [27]. As reported in the same studies, *Conocarpus* biochar (CB) has positive effects on improving soil quality [28]. The results of a study by an international organization have shown, that one of the most polluted cities in the Middle East is Ahvaz [29,30]. Iran is one of the first countries in the world in the field of exploration, exploitation, and transportation of oil, and oil products [31]. Due to the establishment of a considerable volume of waste and cutting of drills in the Middle East, it is necessary to conduct a comprehensive environmental study to reduce and recover this waste [32].

In this study, *Conocarpus* biochar was used as sorbents to remove Cd, Cu, and Zn ions from drilled mud water. The *Conocarpus* biochar samples were obtained by pyrolysis of *Conocarpus* wastes, and their sorption performances were evaluated as the function of initial Cd, Cu, and Zn ions concentration and contact time. The most important characteristics of the region include unique conditions on the coast of the Persian Gulf (southwest of Iran), population boom and rapid industrialization in the last century. The main environmental concerns in this region are the entry of domestic and industrial wastewater and air, dust pollution, from drilling petroleum as wells as contaminants from petroleum and gas industries.

So far, more than 460 oil wells have been drilled in the Ahvaz oil field [33]. Khuzestan soils in oil well drilling areas are contaminated with heavy metals, considering that one of the main concerns of burying drilling waste is the presence of heavy metals [34].

The crude oil production capacity of the Ahvaz field is equal to 150,000 barrels/d. The high volume of drilling in this field causes much environmental pollution, especially heavy metals. This study was carried out in Ahvaz because of the abundance of *Conocarpus* in the region, and the existence of limited research in the literature on stabilizing and immobilizing heavy metals in drilling mud of the Ahvaz petroleum field. *Conocarpus* biochar was used for evaluation of its effects on chemical forms, distribution and stabilization of heavy metals (Cd, Cu, and Zn) in drilling cutting as well as characterization of the reduced partition index (IR), chemical forms and mobility factor (MF) at different incubation times.

Accordingly, this study aimed evaluate the thermodynamics and removal process of heavy metals of drilled mud water and select a better model of absorption isotherm by using *Conocarpus* waste biochar (CW biochar) on the reduced IR, and MF of heavy metals (Cd, Cu, and Zn) in the drilling mud in the Ahvaz petroleum field, the southwest of Iran investigated in 2019.

2. Materials and methods

2.1. Description of study area

Samples were collected in the spring of 2019 from Aghajari Formation at a depth of 1,080 to 1,250 m through well A_{474} in Ahvaz field, in southwest Iran [35] (Fig. 1). Geographically, this area is part of Khuzestan Province. Its capital and only city is Aghajari. Aghajari is connected to the Maroun River through a ground road. The geographic coordinates of the Aghajari are N326 in the southeast, and N310 in the northwest. A sampling of drilling waste (mud + drilling shards) was acquired according to the drilling schedule of oil wells and in coordination with the geological survey of oil-rich areas (Karun) from two wells (Wa (depths: 1,250–1,080 m) – Wb (depths: 2,000–2,050 m) located in Ahvaz oil field.

2.2. Sampling, sample preparation, and instrumentation

In this cross-sectional study, the heavy metal-contaminated soil was collected from the Ahvaz oil field, Iran, in 2019. Surface soil layer (0–20 cm) was used for collecting the samples. The soil samples were sieved passing, through a 2-mm screen. The chemical distribution of the metals in the soil was determined using Tessier sequential extraction method during mentioned incubation times, and the reduced IR and MF of the metals were calculated [36].

Six samples were collected with an average weight of 1.5 ± 0.5 g from the lithologies of the formations of each well (three samples from each well). Moreover, a sample of the soil of the region was collected as a control sample from a place that was not exposed to any pollution and, had less contact with petroleum products and, the smoke of machinery used in the drilling industry, located in the opposite direction of the prevailing wind in the region. Samples were randomly collected from a shaker sieve and were then put

Fig. 1. Ahvaz oil field located in the southwest of Iran.

into plastic bags, transferred to a laboratory, air-dried, and kept in an oven at 50°C for 2 h. After being crushed with a plastic hammer, the samples were passed through a 2-mm sieve to increase their uniformity and mixed well to obtain a composite sample. The air-dried samples (≤2 mm) underwent physicochemical analyses. A calibrated multimeter (LUTRON YK-2001CT) was used to determine DC electrical conductivity and pH in a suspension with a 1:5 soil-to-water ratio. The Walkie and Black method was used for measuring the level of organic matter [37].

A standard ammonium acetate method with an acidity of 8.2 was used to measure and calculate cation exchange capacity (CEC) [38] and calcium carbonate equivalent (CCE) by neutralization with hydrochloric acid [39]. The amount of plant-absorbable HM in the samples was measured using the DTPA method and atomic absorption spectrometer [40]. The total level of HM was measured by the acidic acid method with an atomic absorption spectrometer machine [41,42].

In this study the experiments were performed in batch mode. The equilibrium, kinetic and thermodynamic of heavy metals sorption by *Conocarpus* biochars, were carried out with different initial concentrations of the heavy metals (0–200 mg/L) with 0.03 M $NaNO_3$ as a background solution. Also, the effect of pH (4, 5, and 6), ionic strengths (0.01, 0.03, and 0.1 M), background electrolyte solution ($NaNO_3$, $Ca(NO_3)^2$), and temperature (10, 20, 30, 40, and 50^C) were investigated at different times (0–240 m). The biosorbent dose used in this study was (0%, 2%, 5% and 10% w/w for biochar) in the biosorption process.

To study the effect of *Conocarpus* biochar on the chemical forms of Cd, Cu, and Zn in a contaminated drill cutting, an experiment was conducted as a factorial in a completely randomized design in three replications with four levels of adsorbent (0%, 2%, 5%, and 10% for biochar) and four levels of incubation time (1, 2, 4, and 8 weeks).

2.3. Chemical reagents

The initial concentration of the heavy metals (0–200 mg/L) was prepared by dissolving with 0.03 M $NaNO_3$ as a background solution in 1 L of distilled water. In addition, a solution of 0.1 M HNO_3 was used for the correction of the initial solution pH (the effect of pH (4, 5, 6)), ionic strengths (0.01, 0.03, 0.1 M), background electrolyte solution ($NaNO_3$, $Ca(NO_3)^2$). All the chemical reagents were analytically graded and were used as received [4].

2.4. Preparation of *Conocarpus* waste biochar

Conocarpus remains were collected from the parks of Ahvaz city in Khuzestan Province, southwest of Iran and chopped into small pieces, after being dried in the air for 24 h, at 105°C. Then, at a temperature of 500°C in the room of electric furnace, they were placed in oxygen-free conditions for 3 h at 5°C/min. Next, they were converted to biochar and cooled to ambient temperature with a laboratory mill with, a 350 μm mesh.

2.5. Characterizing the biochar produced from Conocarpus waste

The pH and EC electrical conductivity of *Conocarpus* biochar in 1:10 suspension of biochar, and deionized water (w/v) were measured by digital pH meters (WTW inoLab 3856B, Germany), and a conductor (WTW inoLab 1C20-0211, Germany). For this purpose, an extract with a biochar-to-solution ratio of 1:20 was prepared after being shaken for 1 h in deionized water [43]. Afterward, the following characteristics were also measured: the CEC by the modified ammonium acetate method in pH = 7, the amount of ash by the ASTM method D1762-84, the total amounts of carbon, hydrogen, and nitrogen in biochar by elemental analysis (ECS 4010 CHNSO Analyzer), and the special surface of biochar by sodium hydroxide titration (Method Sear's) [44,45]. In this study, the particle structure use was measured by scanning electron microscope (SEM.AIS-2100, 5.0 KV, Republic of Korea).

2.6. Isothermal model of heavy metals adsorption on adsorbents

The most widely used models to explain the relationship between the adsorption of the equilibrium metal (q_e) and the final concentration (C_e) are Langmuir, Freundlich, and Temkin equations [46]. In this study, experimental data with the least-squares optimization method were given a nonlinear model fit with Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich.

$$q_e = q_{\max} \frac{K_L C_e}{\left(1 + K_L C_e\right)} \text{ Langmuir} \quad (1)$$

$$q_e = K_F C_e^{1/2} \text{ Freundlich} \quad (2)$$

$$q_e = B \ln K_T + B \ln C_e \text{ Temkin} \quad (3)$$

$$q_e = q_m = \exp\left(-\beta\varepsilon^2\right),\ \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

(D-R) Dubinin–Radushkevich (4)

The nonlinear fitting of experimental data with the above equations was performed with the Origin Pro program and graphs were drawn using Excel software.

2.7. Determining of thermodynamic parameters

The thermodynamic parameters of the process were calculated by plotting the curve $\ln(q_e/C_e)$ vs. $1/T$.

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

where ΔH in the enthalpy of the process is in kilojoules per mole and, ΔS is the entropy of the absorption process in Joules/Kelvin mol. The slope of the resulting line represents the value of ΔH and the width of the origin represents the parameter ΔS. Gibbs free energy (ΔG) was estimated from the following equations:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\Delta G = -RT \ln\left(\frac{q_e}{C_e}\right) \quad (7)$$

2.8. Efficiency and capacity of adsorption of cadmium, copper, and zinc by biosorbent (biochar)

Element removal efficiency (RE) and element adsorption capacity (q_e) were obtained using the following equations, respectively:

$$\text{RE} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad (8)$$

$$q_e = \left(C_i - C_e\right) \times \left(\frac{v}{m}\right) \quad (9)$$

where C_i and C_e are the initial and final concentrations of the elements (mg/L). q is the number of adsorbed ions (mg/g), m is the adsorbent mass (g) and v is the volume of the solution (L).

2.9. Analytical methods for the determination of heavy metals

The reference technique for the determination of heavy metals is inductively coupled plasma-mass spectrometry (ICP-MS) [47]. The total amount of heavy metals was measured by the acidic acid method by an Atomic Absorption Spectrophotometry (AAS). The samples of heavy metals were placed in the oven, dried at 70°C for 48 h, weighed for dry matter yield, and ground. After being digested using H_2SO_4–H_2O_2 the, the resulting solution was injected into ICP-MS.

2.10. Incubation experiments and analysis

The air-dried samples of the drilling waste (0.5 kg) with different amounts of *Conocarpus* biochar (0%, 2%, 5%, and 10%, w/w) were mixed with three repetitions and, then poured into plastic containers. The amount of deionized water required to reach 60% moisture capacity was added to the waste samples. The sample containers were covered with a perforated lid to expel the gases and incubated at 25°C for 8 weeks. During the incubation period, the sample container was weighed every 5 d and was added to the water required to maintain the moisture content of the samples. Then, at 1, 2, 4, and 8 weeks after incubation, a certain amount of drilling residue was collected from each of the treatments, and the chemical forms of heavy elements were extracted using the sequential extraction method [48]. A summary of the Tessier sequential extraction method showed in Table 1.

2.11. Reduced potential ecological risk (PER)

Eq. (10) expresses the relative binding strength of the metals based on their chemical forms in terms of reduced partition index.

$$C_j^i = \frac{C}{C_j^i} \rightarrow E_j^i = T_n^i \times C_j^i \rightarrow \text{IR} = \sum_i^n E_j^i \quad (10)$$

where IR is the potential ecological risk of all elements C^i is the measured metal level in the soil sample, C_j^i is the baseline reference value of that element, and T_n^i is the toxicity response factor of each heavy metal (Cd, Cu, Pb, Cr, As, Zn, V and Ni are 30, 5, 5, 2, 10, 1, 2 and 5) [49]. Furthermore, E_j^i is the PER factor of each studied element. Moreover, in this equation takes the following values to represent different stages and fractions: (1) exchangeable fraction, (2) carbonate-bound fraction, (3) iron and manganese oxides-bound fractions, (4) organically-bound fraction, and (5) residual fraction. Also, $n = 1$ or 2. Although n could be selected arbitrarily, given $k = 5$ as per Table 1 and $n = 2$, the minimum and maximum values of IR were respectively obtained as 0.04 and 1. With $n = 2$, suggesting a simple square relationship, i in the sequential selective chemical dissolution increases the binding strength of metals [50].

2.12. Mobility factor of metals in drilling waste

Eq. (11) was used to calculate the mobility factor and determine the contamination degree of metals drilling waste [51].

$$\text{MF} = \frac{F_1 + F_2}{F_1 + F_2 + F_3 + F_4 + F_5} \times 100 \tag{11}$$

where F_1 to F_5 denotes the metal content at different stages and fractions of the sequential extraction. The value of the high mobility index indicates relatively high instability and biological availability of heavy metals in the soil [51].

2.13. Statistical analysis

The experiment was performed as a factorial experiment in a completely randomized design with two factors: biochar amount at four levels (0%, 2%, 5%, and 10%) and incubation time (1, 2, 4, and 8 weeks) for each element in three replications. Graphs were drawn using Excel software. The data were analyzed using SAS software and an LSD test at the probability level of 0.05.

3. Results and discussion

3.1. Contaminated drill cutting

The results of physicochemical characteristics of the experimental drilling waste are depicted in Table 2. As observed, the samples had alkaline pH (8.12) and were contaminated with cadmium, zinc and copper. Also, Table 2 illustrates the statistical concentration data for the heavy metals in the soil of the Ahvaz oil field. According to the results, the contents of Zn, Cu and Cd (Total content of metal and DTPA-extractable) were 138 and 35, 507 and 98, 3.68 and 1.38 mg/kg, respectively. The amount of HM was lower than the maximum allowable concentration (MAC) according to the standards of the World Health Organization (WHO) and the Environmental Protection Agency (EPA) other than copper (Table 2) [52,53].

3.2. *Conocarpus* biochar/*Conocarpus* biochar residues

According to the SEM image, *Conocarpus* biochar has an irregular shape with a porous structure. The specific surface area of *Conocarpus* biochar was 61.24 m^2/g. The specific biochar level of maize residues is 61.83 m^2/g [54]. Fig. 2 shows an image of a *Conocarpus* biochar with a scanning electron microscope.

The physicochemical features of *Conocarpus* biochar are compared to those already reported shows in the previous studies in Table 3. The effect of biochar application on soil CEC and EC amount is shown in Table 3. The specific surface area of *Conocarpus* biochar was 61.24 m^2/g (Table 3).

The statistical analysis showed a significant (p-values < 0.05) increase in EC due to the addition of biochar. Corn

Table 1
Tessier sequential extraction method

Stage	Fraction	Solution	Equilibrium condition
1	Exchangeable	1 M NH_4OAc (pH = 8.5)	1 h shaking at 25°C
2	Carbonate	1 M NaOAc adjusted to (pH = 5) with HOAc	5 h shaking at 25°C
3	Iron and manganese oxides	0.04 M $NH_2OH\cdot HCl$ in 20% (v/v) HOAc	5 h shaking at 96°C
4	Organic matter	0.02 M HNO_3 + H_2O_2 30% (pH = 2)	2–3 h shaking at 85°C
		H_2O_2 30% (pH = 2)	3 h shaking at 85°C
		3.2 M NH_4OAc in 20% (v/v) HNO_3	0.5 h shaking at 25°C
5	Residual	HF-$HClO_4$	0.5 h shaking at 95°C

Table 2
The physico-chemical characteristics of the experimental

pH	DC electrical conductivity	Cation exchange capacity	Organic matter	Calcium carbonate equivalent	
	mL/cm	$cmol_c$/kg		%	
8.12	16.85	28	2.6	25	
Total content of metal (mg/kg)			DTPA-extractable (mg/kg)		
Zn	Cu	Cd	Zn	Cu	Cd
138	507	3.68	35	98	1.38

EC: electrical conductivity, CEC: cation exchange capacity, OM: organic matter, CCE: calcium carbonate equivalent.

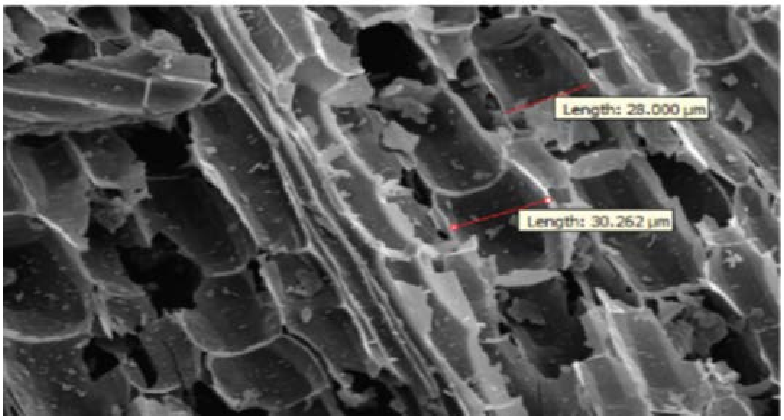

Fig. 2. SEM image of *Conocarpus* waste biochar.

Table 3
Physico-chemical features of *Conocarpus* waste biochar compared to those reported in the literature for other types of biochar

Biochar	Elemental composition (%)				EC	CEC	Ash	Surface area	Reference
	H	N	C	pH	dsm^{-1}	cmol$_c$/kg	%	m^2/g	
Conocarpus waste	2.1	1.92	35	10.4	3.31	22.42	8.2	61.24	This study
Corn residue	1.05	1.56	59.9	9.19	6.3	23.82	33	61.83	[54]
Grape pruning residue	2.9	0.87	71	9.6	0.2	34.4	11.2	277	[55]
Sesame straw	2.1	2.91	72	10.1	–	–	–	289	[56]
Rice straw	1.7	1.66	51	10.1	–	45	42.7	37	[57]

EC: electrical conductivity; CEC: cation exchange capacity.

residue biochar and *Conocarpus* waste biochar with 6.3 and 3.31 dsm^{-1} were the highest mean values of EC (Table 3).

3.3. Effects of Conocarpus biochar on the metal fractionation in drilling cutting

Table 4 demonstrates the concentrations of the chemical sector of Cd in drilling cutting at different incubation durations with different rates of *Conocarpus* waste biochar incorporated.

The distribution of cadmium in different parts of the drilling cutting samples in the control treatment was carbonate (33%) > oxide (26%) > organic (20%) > exchangeable (14%) > residual (7%) (Table 4). The lowercase letter shows the impact of diverse biochar rates on the chemical sector of Cd in drilling cutting.

Means followed by the same letter within a column are not significantly different at p-values < 0.05. In 10% biochar treatment, organic matter transplantation due to the formation of cadmium complexes with organic functional groups at the biochar level increased to 25% and iron and manganese oxide transplantation by 33% after 8 weeks of incubation compared to the control treatment. The reason for the increase in organic matter binding is the formation of cadmium complexes with organic functional groups at the biochar surface (Table 4).

Table 5 shows the concentration of chemical fractions of Zn(II) in cutting drilling with different rates of *Conocarpus* biochar addition at various times of incubation. The exchange and carbonate fraction of zinc was significantly reduced (p-values ≤ 0.05) by adding biochar to the waste samples (Table 5). According to the results, with increasing biochar percentage in waste samples, the amount of zinc exchange fraction decreased from 9% in the control sample to 3% and the carbonate fraction from 23% in the control sample to 13% (Table 5). The lowercase letter shows the impact of diverse biochar levels on the chemical fraction of Zn in DC electrical conductivity and the capital letter compares the impact of biochar at different incubation durations. The mean values followed by the same letter in a column are non-significantly different at p-values < 0.05.

The concentration of chemical fractions of Cu(II) in drilling mud with different rates of *Conocarpus* biochar addition at various times of incubation is shown in Table 6. Means followed by the same letter within a column are not significantly different at p-values < 0.05. The results shows the distribution of copper in different waste sections in the control treatment organically (30%) > residual (24%) > oxide (22%) carbonate (14%) > exchange (11%) (Table 6). The small letter represents the effect of different rates of biochar on the chemical fractions of Cu in cutting drilling. Furthermore, the capital letter compares the effect of biochar at various times of incubation. The lowercase letter shows the impact of diverse biochar levels on the chemical fraction of Cu in DC electrical conductivity, and the capital letter compares the impact of biochar at different incubation durations.

Table 4
Concentrations of the chemical fractions of Cd in drilling cutting with different rates of *Conocarpus* waste biochar incorporated at different incubation durations

Incubation duration	Biochar rate	Fraction				
		EX	CAR	OX	OM	RES
Week	w/w (%)	mg/kg				
1	0	0.51 aA	1.21 aA	0.95 cB	0.73 bA	0.25 aA
	2	0.5 aA	1.19 aA	0.97 bB	0.77 aA	0.26 aA
	5	0.47 bA	1.16 bA	0.99 bC	0.78 aA	0.26 aA
	10	0.4 bA	1.09 cA	1.12 aC	0.8 aA	0.26 aA
2	0	0.49 aA	1.18 aA	0.97 dB	0.74 bA	0.26 aA
	2	0.43 bB	1.14 bB	1.01 bcB	0.81 aA	0.26 aA
	5	0.39 bcB	1.05 cB	1.09 bBC	0.84 aA	0.26 aA
	10	0.36 cB	1 dB	1.12 aC	0.89 aA	0.27 aA
4	0	0.47 aA	1.14 aA	1.01 dAB	0.74 bA	0.26 aA
	2	0.39 bB	1.02 bc	1.09 bcB	0.84 aA	0.26 aA
	5	0.36 cC	1 cC	1.11 bB	0.84 aA	0.26 aA
	10	0.27 dC	0.89 dc	1.16 aB	0.89 aA	0.27 aA
8	0	0.44 aAB	1.11 aAB	1.09 dA	0.73 bA	0.26 aA
	2	0.27 bc	1 bD	1.13 cA	0.8 aA	0.26 aA
	5	0.22 bcD	0.87 cD	1.17 bA	0.8 aA	0.27 aA
	10	0.2 cD	0.59 dD	1.19 aA	0.9 aA	0.27 aA

Table 5
Concentrations of the chemical fractions of Zn in DC electrical conductivity with different levels of CW biochar and diverse incubation durations

Incubation duration	Biochar rate	Fraction				
		Exchangeable	Carbonate	Oxide	Organic matter	Residual
Week	w/w (%)	mg/kg				
1	0	12.91 aA	31.74 aA	50.68 aA	16.78 cA	25.44 aA
	2	11.1 aA	31.74 aA	53.48 aA	17.94 aA	25.44 aA
	5	10.02 aA	28.14 aA	55.11 aA	19.12 aA	26.25 aA
	10	8.14 bA	26.02 bA	56.01 aA	22.02 aA	26.2 aA
2	0	12.12 aA	31.14 aA	51.68 cA	17.12 cA	26.25 aA
	2	9.14 aA	29.1 bB	54.15 bB	18.11 cA	27.3 aA
	5	7.31 bA	25.61 cB	56.12 aA	22.02 aA	27.74 aA
	10	5.63 bA	21.7 cB	58.42 aAB	23.15 aA	28.4 aA
4	0	11.17 aA	30.13 aA	52.62 dA	17.12 cA	27.3 aA
	2	7.84 bA	26.92 Bc	54.82 cAB	19.83 bA	28.5 aA
	5	6.35 cB	22.85 cC	56.73 bA	22.68 aA	28.61 aA
	10	5.62 dB	18.45 dC	59.38 aA	24.82 aA	29.3 aA
8	0	10.1 aA	30.12 aA	53.08 dA	18.05 cA	27.5 aA
	2	6.49 bC	26.7 bD	55.94 cA	20.73bA	27.9 aA
	5	5.61 bD	21.7 cD	58.62 bA	23.42 aA	28.5 aA
	10	4.12 cC	17.43 dD	61.12 aA	25.61 aA	29.3 aA

The mean values followed by the same letter in a column are non-significantly different at p-values < 0.05.

Table 6 shows that after 8 weeks of incubation, the organic matter bonding section went from 147 mg/kg in control treatment to 168 mg/kg in 10% biochar treatment, and the iron and manganese oxide bonding section went from 111.5 mg/kg in control treatment to 119.7 mg/kg in 10% biochar treatment, it increased. The high tendency of

Table 6
Concentrations of the chemical fractions of Cu in DC electrical conductivity with various levels of CW waste biochar at different incubation durations

Incubation duration	Biochar rate	Fraction				
		Exchangeable	Carbonate	Oxide	Organic matter	Residual
Week	w/w (%)	mg/kg				
1	0	55.77 aA	70.98 aA	111.5 aA	147.3 cA	121.6 aA
	2	55.8 aA	70.23 abA	112.3 aB	153.23 bC	121.6 aA
	5	47.4 aA	70.08 bA	112.5 aBC	153.86 bC	121.8 aA
	10	40.3 cA	68.3 cA	116.5 aB	160 aB	121.8 aA
2	0	47.85 aA	71.76 aA	111.63 aA	153.5 cA	121.6 aA
	2	46.57 bB	69.24 bB	113.3 aA	155.8 bC	121.6 aA
	5	45.83 bB	67.3 cB	115.5 aAB	156.3 bC	121.6 aA
	10	44.26 cB	64.12 cA	117.6 aB	159.1 aB	121.6 aA
4	0	45.58 aA	70.08 aA	112.5 aA	155.4 cA	121.6 aA
	2	39.23 bC	68.26 aB	117.5 aAB	159.36 bB	121.6 aA
	5	38.15 bC	66.83 bC	118.83 aAB	161.5 bB	121.6 aA
	10	37.41 Bc	63.13 bB	118.83 aB	163.3 aB	121.9 aA
8	0	43.6 aA	70.08 aA	113.3 bcA	155.6 dA	121.6 aA
	2	37.56 bC	65.12 bBC	118.83 bA	160.3 cA	121.6 aA
	5	36.43 bC	63.14 cC	118.9 bA	162.62 bA	121.9 aA
	10	33.51 cC	61.86 cB	119.7 aA	168.2 aA	121.9 aA

copper to organic compounds and the formation of very stable complexes of copper with organic functional groups at the biochar level is the reason for the increase in the part attached to organic matter.

3.4. Investigation of the effect of different values of Conocarpus biochar on metal index of mobility factors (MF) in drilling waste samples

Fig. 3 shows the relative index of metal mobility (MF) of Cd (a), Zn (b), and Cu (c) with different rates of *Conocarpus* biochar application at various incubation times. The components that determine the environmental risk among the chemical forms of heavy metals are the exchange and carbonate. Therefore, the effect of soil conditioners on the immobilization of heavy metals in contaminated soils can be investigated by evaluating the changes in the exchange and carbonation of HM. At each level of biochar added to the soil, the percentage of elements in the first and second extracts in the sequential extraction process was used as the mobility factors. According to the index of mobility factors, metal mobility is classified into four categories low (10% ≤ MF ≤ 1%), medium (30% ≤ MF ≤ 10%), high (30% ≤ MF ≤ 50%), and very high (<MF 50%) [58]. Mobility and bioavailability tests for heavy metals can precisely identify the potential environmental impact of waste [59].

The lowest amount of MF was observed in 10% biochar treatment 8 weeks after incubation. mobility factors for Cd, Zn, and Cu compared with the control sample decreased to 16, 25, and 19, respectively. Such a decrease, indicates the formation of a stable metal-biochar complex (Fig. 3).

Król et al. [59] in their study reported that Cd was the most mobile element among the analyzed elements. On the other hand, Cr was characterized by very low mobility. Verla et al. [60] studied the relationship between mobility factors of selected heavy metals and soil particle size in soils. Their results revealed that Cu and Zn were the most mobile elements, while Cu was the least mobile element [60].

It is possible that weak electrostatic bonds in cadmium may affect its high mobility index in waste samples. This finding agrees with the result of a study conducted on the effect of equilibrium solution ionic strength on the adsorption of Zn, Cu, Cd, Pb, As, and P in an aluminum mine by Costa et al. [61]. Adding biochar to drilling waste samples reduced the metal mobility index as Zn > Cu > Cd.

The distribution of Zn in different parts of the waste sample in the control treatment was oxidized (37%) > carbonate (23%) > residual (19%) > organic (12%) > exchangeable (9%), which after 8 weeks after the onset of incubation in 10% biochar treatment, it changed to oxide (44%) > residual (21%) > organic (19%) carbonate (12%) > exchange (3%). These results prove that biochar reduces the bioavailability of zinc to an appropriate degree in contaminated soils as also reported by Zahedifar [62].

The highest IR value for Cu was observed in 10% biochar treatment the application of the biochar significantly (p-value ≤ 0.01) decreased the exchangeable and carbonate fractions and increased iron and manganese oxides bound fractions of the metals in comparison to the control treatment. The IR Values increased and MF values decreased with an increase in biochar levels and incubation time indicating a decrease in the mobility of metals in the soil. Thus, it can be concluded that the addition of biochar in drill cutting leads to a transformation of the metals from unstable forms (exchangeable and carbonate forms) to stable forms (iron and manganese oxide bound and residual forms), and

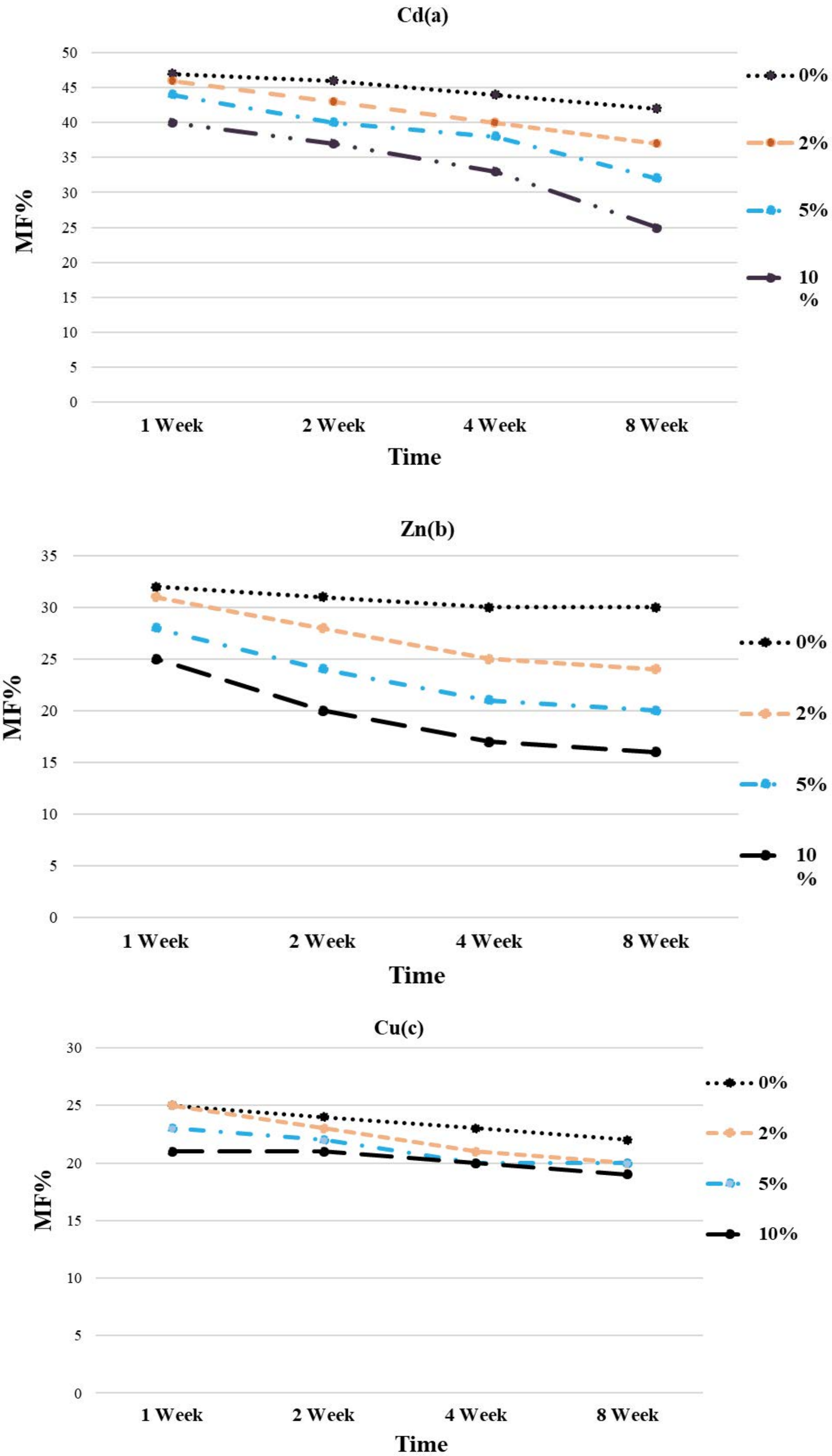

Fig. 3. Relative index of mobility factors (MF) of Cd (a), Zn (b), and Cu (c) with different rates of *Conocarpus* biochar application at various incubation times.

consequently decreases the mobility of metals in drill cutting. The results of this study showed that biochar deforms metals from unstable to stable forms, thus reducing the environmental risk of heavy metals.

As the sole measurement of the concentration of total heavy metals in the environment does not necessarily determine their degree of pollution and cannot be a suitable criterion for accurate assessment of heavy metal contamination in soil, the bioavailability potential of metals for plants and the rate of metal mobility in soil are used. In addition to examining their total concentration, they help understand the potential effects of metals on living systems and sources of current pollution [63,64].

The results of this study showed that the concentration of Cd, Cu, and Zn in pH = 8.12 were 3.68, 507, and 138 mg/kg, respectively. Ionic strength and pH of the background solution significantly affected metals adsorption, and the highest adsorption capacity was obtained at pH 6, with ionic strengths of 0.01 M at 50°C with $NaNO_3$ as a background solution.

In this study, the results demonstrated that the specific surface area of *Conocarpus* biochar was 61.24 m^2/g. In 2% and 10% biochar treatment, cadmium exchange fraction increased from 0.27 to 0.2 mg/kg and cadmium carbonate fraction from 1 to 0.59 mg/kg after 8 weeks. *Conocarpus* biochar also had an alkaline pH (10.3). Adding 10% biochar increased the pH of the waste samples from 8.12 to 8.71 and 9.82 after 4 and 8 weeks of incubation.

Park et al. [65] evaluated the adsorption of heavy metals in mono and multi-metal forms onto sesame straw biochar. According to their report, biochar sesame skin residues have a pH (10.1) [65] which is consistent with the findings of this study. Increasing soil pH can increase the hydrolysis of metal cations and the formation of metal deposits in the form of oxides and metal hydroxides, which leads to a decrease in the exchange and carbonate fraction [66].

3.5. Evaluation of the effect of different values of Conocarpus biochar on the reduced partition index or stability index (IR) in waste samples

The index of metal stability (IR) of Cd, Cu, and Zn with different rates of *Conocarpus* biochar application at various incubation times is shown in Fig. 4. The IR index is used to quantify the relative bond strength of metals in different soils or different metals in soil. In general, low IR values (values close to the minimum) indicate a pattern of distribution in which most of the metal is in the soluble and exchangeable components, while high IR values (values close to 1) are due to the high share of metals in the remaining component [50]. Intermediate values represent a pattern in which the metal is relatively distributed among all solid phase components. IR index is affected by pollution levels, type of pollution and soil characteristics [50]. At the beginning of the incubation period and in the control treatment, the amount of reduced partition index decreases as Cd > Zn > Cu, which indicates a strong bond of copper with the solid phase of the soil and a weak bond of cadmium, resulting in high bioavailability of cadmium in the soil (Fig. 4). By increasing the percentage of biochar added to the waste samples and after eight weeks of incubation, the IR value for metals significantly increased from 0.34 to 0.43 for Cd, from 0.43 to 0.51 for Zn, and from 0.53 to 0.56 for Cu, which indicates the increase in the amount of metal in the stable fraction (the moieties attached to the organic matter and attached to the iron and manganese oxides) with increasing biochar and incubation time (Fig. 4).

Based on the result of the study, due to the calcareous nature of the waste samples, the carbonate form was the most measured form of cadmium. The exchange and carbonate fraction of cadmium decreased with increasing biochar percentage and incubation time. Biochar with a high specific surface area and porous structure has a high ability to immobilize heavy elements. The performance of biochar in increasing soil acidity and reducing the bioavailability of HM has been reported in the literature [67,68].

Thus, it can be concluded that the use of Zn biochar increases the bond fraction with iron and manganese oxides by 44% in the 10% biochar treatment. Adding biochar to waste samples increases the pH and thus increases the adsorption of metals on oxides.

Gusiatin and Kulikowska [69] reported that iron and manganese oxides have a high affinity for zinc and are distributed in biochar-treated soils with high Zn acidity from the exchange and carbonate section to the bonding section with iron and manganese oxides. Besides, in agreement with the findings of this study, the increase in organic matter binding may be due to the increase in dissolved organic ligands attached to zinc complexes [69].

Based on the results of this study, the organic form showed the highest measured form of copper in the control treatment. After 8 weeks of incubation, the exchange and carbonate fraction were significantly converted to the bond with organic matter and iron and manganese oxides ($p \leq 0.05$). Also, the distribution of copper in different parts of the waste sample in the 10% treatment changed to organic (33%) > residual (24%), oxide (24%) > carbonate (12%) > exchange (7%). This result agrees with the result of Gusiatin and Kulikowska [69].

Lucchini et al. [70] showed that ash accretion, dissolution of hydroxides, and carbonates are the main advantages of using biochar in soil, similar to the findings of this study. In 2009, Nguyen and Lehmann in the USA assessed the effects of water regimes and differences in biomass-derived black carbon materials [71]. Their report showed that increasing soil pH can be performed by using the release of biochar alkalinity [71]. Another study by Al-Wabel et al. [28] showed that applying biochar significantly reduced the level of HM in maize plants. The highest decrease in heavy metal concentrations was 28% for Zn, 60% for Cu, and 53.2% for Cd.

3.6. Isotherm and kinetics models

The isotherm and kinetics modeling of experimental data has been done to have a deeper understanding of the dynamics of Cd, Zn, and Cu sorption processes on these types of biochars and to obtain information on the sorption rate. Table 7 demonstrates the kinetic parameters calculated from the mathematical equations of each kinetic model.

The pseudo-second-order model (R^2 = 0.99–1.00, p-values ≤ 0.01) as compared to the pseudo-first-order model (R^2 = 0/53–0/71, p-values ≤ 0/01), Elovich (R^2 = 0/94–0/97,

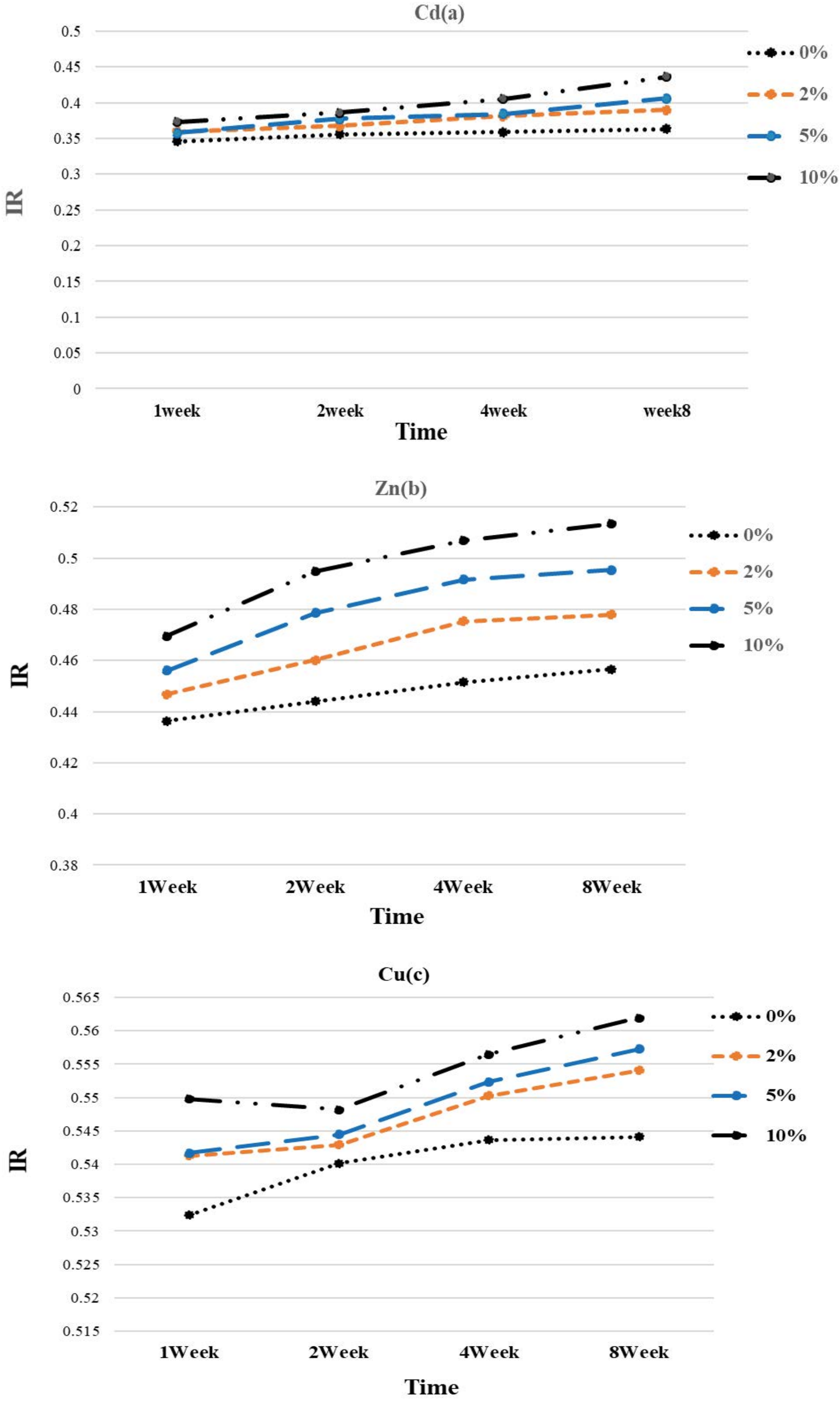

Fig. 4. Index of metal stability (IR) of (a) Cd, (b) Zn, and (c) Cu with different rates of *Conocarpus* biochar application at various incubation times.

Table 7
Kinetic parameters for the sorption of Cd, Zn, and Cu ions on the *Conocarpus* biochar

Kinetic models	Fixed coefficients of the model	Cd	Zn	Cu
	k_1 (g/mg min)	0.12	0.09	0.09
Pseudo-first-order model	q_e (mg/g)	1.9	1.1	2.2
	R^2	0.60	0.53	0.54
	k_2 (g/mg min)	0.26	0.40	0.20
Pseudo-second-order model	q_e (mg/g)	9	4.9	9.2
	R^2	1	1	0.99
	α (mg/g min)	6.7×10^8	8.7×10^9	1.9×10^8
Elovich	β (mg/g)	0.31	0.15	0.33
	R^2	0.97	0.95	0.96
	a	7.6	4.1	7.5
Exponential function	B	0.04	0.03	0.04
	R^2	0.97	0.96	0.97

p-values ≤ 0/01) and exponential function (R^2 = 0/93–0/97, *p*-values ≤ 0/01) has a better fit (Table 7). Among adsorption kinetic models, the pseudo-second-order model was better fitted for the experimental data (R^2 = 0.99–1.00, *p*-values ≤ 0.01) (Table 7). The comparison of velocity coefficients k_1 and k_2 for pseudo-first-order and pseudo-second-order models for biochar showed that the rate of adsorption of elements on biochar was fast (Table 7).

The result of the study also revealed that the application of *Conocarpus* waste biochar could be safely used in drill cutting because the concentrations of metals did not increase. The results showed that the removal efficiency and adsorption capacity of adsorbents decreased with increasing initial concentration.

The results of the regression study (R^2) of adsorption models showed that the Langmuir and Dubinin–Radushkevich equations fit lead and copper adsorption data better, and the Langmuir and Freundlich equations fit the cadmium, zinc, and strontium adsorption data better similar to the Langmuir equation. The results showed the best fit with barium adsorption data. The Langmuir isotherm coefficient (mg/g) q_{max}, expresses the maximum amount of monolayer adsorption under the conditions of complete saturation of adsorbent surfaces. A comparison of the maximum monolayer adsorption of Langmuir (q_{max}) at different ionic strengths showed that with increasing the ionic strength of solution from 0.01 to 0.1 caused q_{max} on Cd 46 to 30, Pb 65 to 45, Cu 50 to 39, Zn 35 to 27, Sr 63 to 49 and Ba 56 to 38 mg/g in biochar *Conocarpus* decreased. Results also showed that the q_{max} coefficient was high in all three ionic strengths for the *Conocarpus* biochar, which can be attributed to the specific surface area and high cation exchange capacity of the *Conocarpus* biochar. Another coefficient of the Langmuir experimental model is K_L (L/mg), which depends on the adsorption energy. In this study, K_L values also decreased as the ionic strength of the solution increased.

The sorption energy parameter (E) of Dubinin–Radushkevich isotherm and negative Gibbs free energy (ΔG) values indicated the physical and spontaneous sorption reaction of the metals by the sorbent. The separation factor of Langmuir (R_L) indicated that the sorption reactions of metals by the sorbent are favorable (R_L = 0.01–0.50). According to the results, the index of mobility factors for cadmium and copper were 47%, 32%, and 25%. This amount indicated that the highest environmental risk was for Cd, Zn, and Cu, respectively.

Dobaradaran et al. [23] investigated the isotherms and biosorption kinetics biosorption of fluoride by *Padina sanctae-crucis* algae. They reported that the Freundlich model was a better fit than the Langmuir model, showing heterogeneous biosorption surface and the possibility of multilayer biosorption of fluoride by biosorbent [23].

Adsorption isotherms are one of the important factors in the design of adsorption systems. In fact, the adsorption temperature describes how the adsorbent and the adsorbent interact. Therefore, it is always considered a basic factor to determine the capacity of an adsorbent and optimize the absorber consumption.

The Langmuir model fit the adsorption data better. The sorption capacity factors (q_{max}, K_F, K_T, q_D) and sorption energy factors (n, K_L, B) of biochar were also calculated. Metal sorption by *Conocarpus* biochars was as Cu > Cd > Pb > Zn > Sr > Ba. Kaur and Rani [72] conducted a study in 2006 in Delhi and reported that the bioavailability of metals was higher than the limit defined for Cd, Cu, and Zn: 0.5, 5, and 10 mg/kg, respectively). These results are similar to the findings of the present study only for Cu.

4. Conclusion

The results showed that the pH of drill cutting samples was studied as alkaline and because many heavy metals are immobile or inactive under these conditions, their concentration in drilling waste increased. The biochar samples were obtained by pyrolysis of *Conocarpus* wastes at relatively low temperatures (50°C for 2 hr), and a better model of absorption isotherm in drilled mud water was selected. In conclusion, the addition of *Conocarpus* biochar at the highest rate (10%) as a low-cost modifier to drilling waste can lead to the deformation of Cd, Cu, and Zn from unstable forms (exchangeable and carbonate forms) to stable forms (forms bonded with iron and manganese oxides and organic form) as a result of reducing the mobility of these metals in the drilling waste. Also, the results of this study showed that exposure to heavy metals can cause problems for animals, human health, and the environment.

The results also revealed that the use of *Conocarpus* biochar caused a significant decrease in the studied elements in the exchange and carbonate sections and a significant increase in the elements in the sections bonded with organic matter and iron and manganese oxides compared to the control sample while it had no significant effect on the remaining section (p-value ≤ 0.05). In addition, it seems that the high level of heavy metals in drill cutting by the can be caused gas and petroleum industries. As the percentage of biochar added to the residue and incubation time increased, the IR value rose and the MF value decreased. The addition of biochar enhanced the stability of metals in Cu > Zn > Cd, respectively. Finally, the addition of biochar to the soil reduces the mobility of cadmium, copper, and zinc in contaminated drilling waste in the short term. However, the application of the findings of this study requires a long-term study in the field and a better understanding of the interaction between drilling debris and *Conocarpus* biochar.

Conflict of interests

The authors have no conflict of interest.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Authors contributions

Zohre Lajmiri Orak, Sima Sabzalipour*, Ebrahim Panahpour, Sina Attar Roshan, Haman Tavakkoli S S designed and performed experiments, analyzed data, and co-wrote the paper. Z L O, E P, HT performed experiments and prepared the figures and co-wrote the paper.

E P Investigation, Methodology; writing – review and editing. S A R; Software; writing – review and editing, arranged the ethical approval and gathered data. All authors read and approved the final manuscript.

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Ethical approval

This study was originally approved by the Islamic Azad University, Ahvaz Branch Ph.D. thesis of Zohre Lajmiri Orak with code number 162407606.

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