Research Paper

Chemical Fractionation of Copper and Zinc After Addition of Conocarpous Waste Biochar to A Drill Cutting

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Citation Lajmiri Orak Z, Sabzalipour S, Panahpour E, Attar Roshan S, Tavakkoli H. Chemical Fractionation of Copper and Zinc After Addition of Conocarpous Waste Biochar to A Drill Cutting. Journal of Advances in Environmental Health Research. 2021; 9(1):57-68. http://dx.doi.org/10.32598/JAEHR.9.1.1202

doi: http://dx.doi.org/10.32598/JAEHR.9.1.1202

Article info:
Received: 05 Dec 2020
Accepted: 15 Mar 2021
Publish: 01 Jan 2021

Keywords:
Biochar, Immobilization, Mobility, Zinc, Copper

ABSTRACT

Background: Drill Cutting (DC) are large amount of waste generated in gas and oil exploration and production activities that contains toxic substances, especially heavy metals. This study aimed to use Conocarpus Waste (CW) biochar to investigate its effects on changes in chemical forms and stabilization and distribution of Cu and Zn in DC samples of Ahvaz oil field at different incubation times.

Methods: In order to study the effects of CW biochar at different rates (0, 2, 5, and 10% w/w) and four incubation times (1, 2, 4, and 8 weeks) for adsorption and chemical fractionation of Copper (Cu) and Zinc (Zn) in DC of Ahvaz oil field in southwestern Iran. An experiment was conducted as a factorial in a completely randomized designing in three replication. Sequential extraction procedure of Tessier was applied for the determination of heavy metals fraction.

Results: Application of biochar significantly ($P<0.05$) increased the pH, soil organic carbon (SOC), electrical conductivity (EC), and cation exchange capacity (CEC) especially at the 10% application rate. After the addition of CW biochar, the exchangeable (EX) and carbonate (CAR) fractions of Cu and Zn, respectively decreased ($P\leq0.05$) significantly while organic matter (OM) bound, oxides (OX) bound, and residual (RES) fraction were increased.

Conclusion: The CW biochar can be a low-cost and effective amendment in immobilizing the Cu and Zn, and also effectively to reducing their mobility in DC.

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1. Introduction

Drill Cutting (DC) refers to a large amount of waste generated in gas and oil exploration and production activities that contain toxic substances, especially heavy metals. They have potentially adverse effects on the ecosystem [1]. Heavy metal in different parts of the drilling industry can enter the environment and have different effects [2]. In many oil-producing countries, however, DC around gas and oil drilling equipment are dumped on-site, and over time it can seriously damage agriculture in the surrounding areas and aquatic ecosystems [3]. In recent years, environmentally friendly and inexpensive methods have been used to reduce the mobility and bioavailability of heavy metals in contaminated soils.

Meanwhile, adsorption by soil conditioners is one of the newest inexpensive methods [4]. According to studies, biochar is one of the effective substances in adsorption and reduction of soil heavy metal pollution in situ and management [5]. Biochar is a carbon-rich material with a highly porous structure that is prepared with thermal decomposition of biomass under limited or free oxygen conditions [6]. Because of its high specific surface area, porous structure, active functional groups, high Cation Exchange Capacity (CEC), and high pH, biochar has a high potential for stabilization of heavy metals compared to the main biomass [7, 8]. Copper (Cu) and zinc (Zn) are elements present in DC. These elements are highly biological and were essential for the functioning of living organisms. However, when these metals are higher than the normal amount, they are considered a challenge and a serious threat to the environment.

It should be noted that excess amounts of heavy metals in the environment as a harmful substance leads to tissue damage and, even in many cases, to the death of living organisms. Heavy metals can move and change form in the soil [7]. Investigation of the relationship between heavy metals and their chemical sequence with geochemical properties of soil leads to understanding the distribution of different forms of heavy metals, their toxicity and mobility in soil and can affect the distribution of various forms of heavy metals from exchangeable fractions to a non-exchangeable fraction in contaminated soils [9]. Many studies have shown that biochar has a high potential to convert varying forms of heavy metals into a stable form, ultimately reducing their mobility and bioavailability in soil [7, 8]. Gholami et al. examined the effect of biochar on the chemical form and adsorption of heavy metals. They reported that the use of biochar has positive effects on stabilizing heavy metals by reducing their mobility in soil [10]. Furthermore, Hamzenejad Taghlidabad and Sepehr reported that the application of biochar of grape pruning residues significantly reduces the elements in the exchangeable and carbonate fraction and significantly increases the elements in Organic Matter bound (OM) and Oxides bound (OX) fraction in the soil [11]. Gholami and Rahimi, in a study, using sequential extraction method, and Tessier et al. [12, 13] stated that the use of different levels of carrot pulp in contaminated soil reduces the Exchangeable (EX) and Carbonate (CAR) fraction of Cu and Zn but OX, OM and Residual (RES) fraction increase. Also, pH, Electrical Conductivity (EC), and CEC in the soil increased with the application of biochar [13]. The effect of conocarpus biochar on different forms of Cu and Zn in DC of Ahvaz oil field in Iran has not been investigated. Therefore, this study aimed to use Conocarpus Waste (CW) biochar to investigate its effects on changes in chemical forms, stabilization, and distribution of Cu and Zn in DC samples of the Ahvaz oil field at different incubation times.

2. Materials and Methods

Physicochemical analyses of cutting drilling

According to Figure 1, samples were collected in April and May 2019 from Ahwaz Formation at a depth of 1550 to 1650 m and well No. A_1 in Ahvaz oil Field, Khuzestan Province in the southwest of Iran. Five samples were randomly collected from a shale shaker and were inserted into plastic bags, transferred to a laboratory, dried in the air, and then kept at 50ºC in an oven for 2 hours. After being crushed with a plastic hammer, these 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, and a calibrated multimeter (LUTRON YK-2001CT) was used to determine EC and DC pH in a suspension with a 1:5 soil-to-water ratio. The Walkley-Black technique was employed to find organic matter [14], and CEC of DC samples were measured by using sodium acetate (NaOAc 1M, pH=8.2) [15]. Rapid titration was also utilized to obtain the total carbonate as calcium carbonate equivalent [16]. Atomic absorption was also used to measure the total amount of heavy metals. Besides, flame atomic absorption spectrometry was conducted to specify the DTPA-extractable content of these heavy metals [17].

Biochar production

In this study, CW biochar was used due to the high volume of conocarpus pruning in the urban green area.

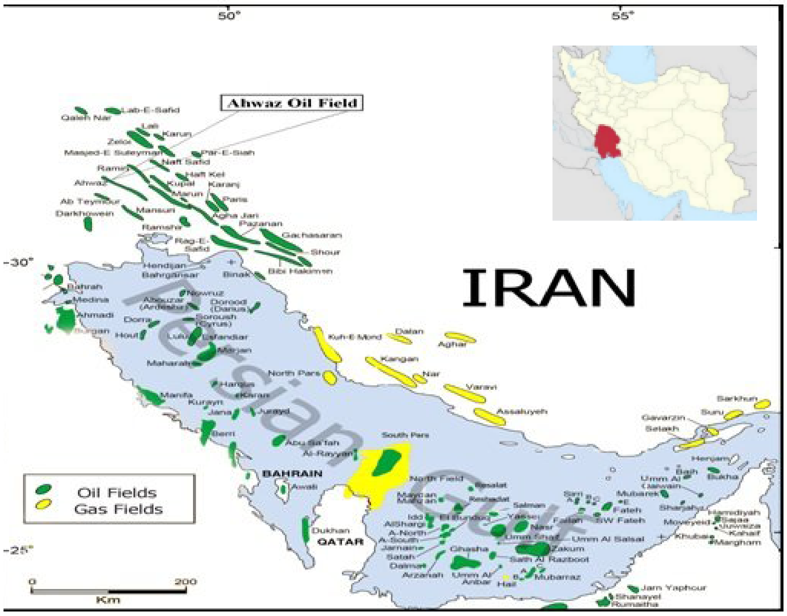

Figure 1. Ahvaz oil field in the southwest of Iran [18]

Conocarpus wastes were collected and dried in an oven at 105°C and then ground and passed through a 2-mm sieve. Afterward, slow pyrolysis was performed, followed by heating to 500ºC for three hours in an electrical furnace at a heating rate of 5ºC/min. The flow of nitrogen was utilized to protect the feedstock against free oxygen and preserve the anoxic status [19]. The resulting black residue was then cooled to room temperature and passed through a 500-µm mesh.

Characterizing the biochar produced from conocarpus waste

In this study, Soil Organic Carbon (SOC) using wet oxidation method [20], along with pH and EC of conocarpus biochar in 1:10 suspension of biochar and deionized water (w/v) [21], were measured using a digital pH meter (WTW inoLab 3856B, Germany) and a conductivity meter (WTW inoLab 1C20-0211, Germany), respectively. Moreover, a modified ammonium-acetate method was used to evaluate the CEC in biochar [22]. The ash content was also measured using the ASTM D1762-84 method. Total carbon, nitrogen, oxygen, and hydrogen contents in the biochar were also determined using an elemental analyzer (ECS 4010 CHNSO Analyzer). Sear's method was used to determine the specific surface area in biochar [23]. The morphology of the adsorbent surface was determined using a scanning electron microscope (SEM, AIS-2100, 5.0 kV, Republic of Korea).

Incubation experiments and analysis

Air-dried DC samples (0.5 kg) were placed in polyethylene cups and mixed with different rates of CW biochar (0%, 2%, 5%, and 10%, w/w) and then wetted with deionized water up to 60% of the water holding capacity on the farm. Then all the cups were covered with a perforated plastic lid to allow the exchange of gases and less moisture to be lost. Subsequently, the samples were incubated completely randomly and in a factorial way in three replications for eight weeks at a temperature of 25°C. Cups containing the treatments were weighed every 5 days, and distilled water was added to them during the incubation period to maintain the necessary moisture. Subsamples of each cup were collected periodically after 1, 2, 4, and 8 weeks for sequential extraction by the Tessier method [12, 24]. Table 1 summarizes the Tessier sequential extraction procedure.

Statistical analyses

This experiment was designed as factorial and 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) in three repetitions for each metal separately. Also, the means were compared with the Least Significant Difference (LSD) test at the level of 5% probability that was done with the SAS (9.1) software, and graphs were drawn using Excel software.

Table 1. Summary of the Tessier sequential extraction procedure used in this study [24]

Steps	Fractions	Solutions	Equilibrium Conditions	Time, h
1	Exchangeable (EX)	NH_4OAC, 1 M (pH=8.5)	Shaking at 25°C	1
2	Carbonate (CAR)	NaOAc, 1 M adjusted to pH 5.0 with HOAC	Shaking at 25°C	5
3	Fe & Mn Oxides (OX)	$NH_2OH.HCl$, 0.04 M in 20% (v/v) HOAC	Shaking at 96°C	5
4	Organic Mtter (OM)	HNO_3, 0.02 M+ H_2O_2 30% (pH=2) H_2O_2 30% (pH=2) NH_4OAc, 3.2 M in 20% (v/v) HNO_3	Shaking at. 85°C Shaking at. 85°C Shaking at. 25°C	2-3 3 0.5
5	Residual (RES)	$HF-HClO_4$	Shaking at 95°C	0.5

3. Results and Discussion

Drill cutting and biochar characterization

Some physicochemical properties of the drilling waste samples studied are presented in Table 2. The pH of DC samples was in the alkaline range (pH=8.12). The amount of Cu element was higher, and the amount of Zn was less than their permissible concentration according to the standard of the Environmental Protection Agency (EPA) and the World Health Organization (WHO) (maximum permissible concentration for Cu, 35 mg/kg and for Zn 500 mg/kg [25, 26]. The study of bioavailability concentrations of metals and the rate of metal mobility in soil, along with the study of their total concentrations, is effective in understanding the potential effects of metals on ecosystems and sources of pollution. According to Kaur and Rani, the allowable bioavailability limit for Cu is 5 mg/kg and for Zn is 10 mg/kg [27]. In this study, the bioavailability of these metals is higher than the allowable limit defined for them.

Conocarpous waste biochar

Figure 2 shows an image of a CW biochar with a Scanning Electron Microscope (SEM). SEM was used for the observation of the morphology of CW biochar. The image was obtained at 1000X magnification. Some physical and chemical properties of CW biochar are listed in Table 3. In this study, the specific surface area of CW biochar was 61.24 m^2/g (Table 3). Moreover, a specific surface area of 61.83 m^2/g was calculated for corn residue [28]. CW biochar also has an alkaline pH (10.3). According to a report by Park et al., biochar sesame residues have a pH of 10.1 [4], which is consistent with the results obtained in this study.

Effect of conocarpous waste biochar on cutting drilling properties

Physicochemical changes of DC samples in different biochar treatments and different incubation times are shown in Figure 3. The pH of DC samples changed from 8.12 in the control sample to 10.15 in 10% biochar treatment after 8 weeks of incubation. The pH value increased from 25% to 26.81% in 5% and 10% biochar treatments compared to the control sample (Figure 2A). With increasing soil pH, the absorption of heavy metals by carbonate colloids and soil hydroxides increases, and as a result, the bioavailability of heavy metals in the soil decreases [7]. Increased soil acidity after the addition of biochar has been shown in many studies. It can be due to ash containing mineral compounds in the form of carbonate or oxide, which, when dissolved in water, can create an alkaline state in the environment [30]. The EC of the samples increased by 20% and 29% in the 5% and 10% biochar treatments after eight weeks of incubation compared to the control sample (Figure 3B). Appliction

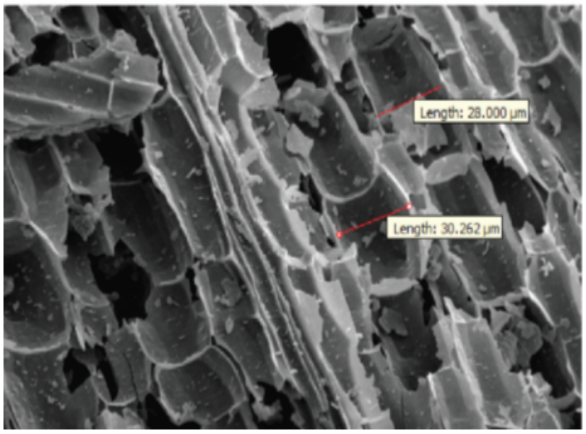

Figure 2. Scanning Electron Microscopy (SEM) Images of CW biochar [29]

Table 2. Some physicochemical characteristics of the experimental drilling cutting

EC	CEC		CCE	OM
1 ds/m	Cmolc/kg	pH	%	%
31	28	8.12	55	3.6
Total metal (mg/kg)			DTPA-extractable (mg/kg)	
Zn	Cu		Zn	Cu
97	301		21	16

EC: Electrical Conductivity; CEC: Cation ExchangeCapacity; OM: Organic Matter; CCE: Calcium Carbonate Equivalent.

of biochar increased CEC in DC samples (Figure 3C) so that CEC samples increased from 28 in the control sample to 34 and 38 in the 5% and 10% treatments after 8 weeks. CW biochar increased the CEC value from 18.88% to 31.18%. In general, the increase in CEC of DC samples is due to the high presence of carboxylic and carbonyl functional groups in the biochar surface as well as the high specific surface area and especially the porous structure in the biochar [31]. The use of biochar can increase the pH and CEC in the soil, consistent with the results obtained in this study [13, 19]. The amount of organic carbon in the treatment of 5% and 10% of biochar increased from 4.62 to 4.91 compared to the control treatment after 8 weeks, respectively (Figure 3D), which is similar to the study of Karimi et al. [28].

Chemical forms of Cu and Zn in DC amended by CW biochar

Exchangeable fraction

As shown in Figure 4A, the EX fraction of Cu decreased from 4.06% in the control sample to 1.9% and 1.7% in the 5% and 10% biochar treatment in the eighth week (Figure 4A). EX fraction of Zn decreased from 5.2% in the control sample to 1.8% and 1.1% in 5% and 10% biochar treatments in the eighth week (Figure 5A), which is consistent with the results of a study by Dang et al. [32]. The amount of EX fraction of Zn and Cu in all treatments of CW biochar and at different incubation times were significantly different from the control treatment. EX fraction of Zn and Cu decreased in 10% biochar treatment in all incubation times. This decrease may be due to increased SOC, CEC, and pH after applying CW biochar [33]. Thus, pH is one of the most important properties of soil on the bioavailability of heavy metals [34]. Increasing the pH leads to increased hydrolysis of heavy metals in the soil, and besides, high pH increases the levels of negative surface charge. However, the increase in adsorption of metal hydroxides is greater than the free form of metal ions in the soil [7], which reduces the amount of heavy metals in the EX fraction in the soil. Also, increasing the CEC of DC samples in different treatments of CW biochar causes ionic complexes of metals with biochar, and the increasing SOC after the application of CW biochar leads to an increase in stable organic complexes with heavy metals, that ultimately decrease the metal content in the EX forms [10].

Table 3. Properties of CW biochar

Properties		Properties	
Surface area (M2/g)	61.24	C (%)	78
Ash (%)	8.2	H (%)	2.1
pH	10.3	O (%)	22
CEC (Cmolc/kg)	27	N (%)	0.72
EC (ds/m)	3.31	-	

CEC: Cation Exchange Capacity; EC: Electrical Conductivity.

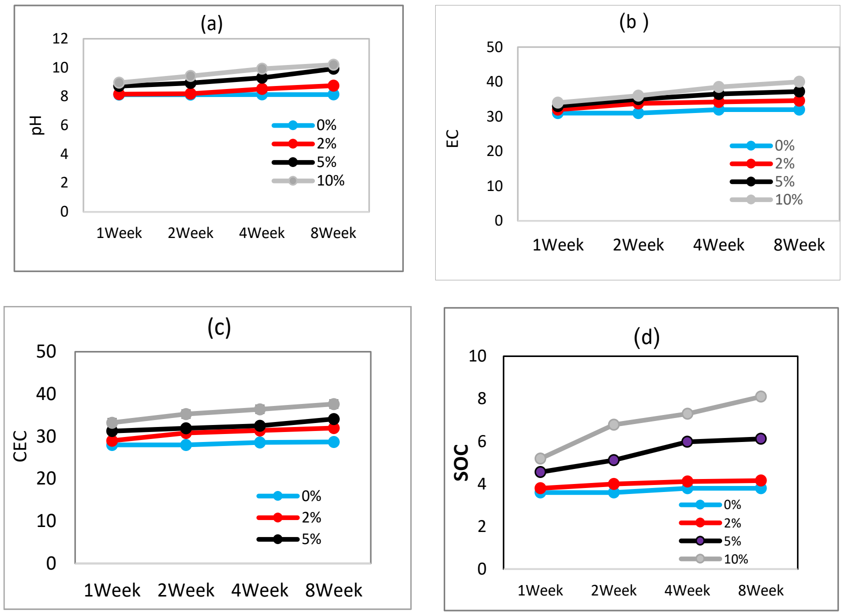

Figure. 3. Amendment effect on soil properties: pH(a), Electrical Conductivity (EC) (b), Cation Exchange Capacity (CEC) (c), Soil Organic Carbon (SOC) (d)

Carbonate fraction

The CAR fraction of Cu in treatments of 5% and 10% was significantly reduced compared to the control sample so that its rate increased from 4% in the control sample to 1.5% in the 10% biochar treatment after 8 weeks, which was reduced by 2.5%. With a control sample in the first week (Figure 4B), according to Figure 4 (b) and 5 (b), there was a significant difference between the amount of Cu and Zn in the CAR fraction in different biochar treatments. Also, the CAR fraction of Zn decreased from 22% in control to 12.37% in 10% biochar treatment in the eighth week, which is consistent with the research of Hamzenejad Taghlidabad and Sepehr [11]. In this study, the reduction of Cu and Zn concentrations in CAR and EX fractions in different biochar treatments indicates that these treatments could convert Zn and Cu into more stable forms. The bonded form of the elements with carbonates is known as almost accessible. Because under the influence of pH may be solved and increase their bioavailability. Also, increasing SOC with the use of biochar has a very significant role in reducing the CAR fraction of heavy metals in the soil. The reduction of CAR form concentration compared to the control in 5% and 10% treatments for Cu was 2.04% and 2.36% and for Zn were 7.99% and 9.66%, respectively. In general, at all levels of CW biochar, biochar application decreases the concentrations of Zn and Cu in the CAR fraction and ultimately reduces the available form of them in contaminated soils.

Fe and Mn oxides fraction

Absorption and co-precipitation of Cu with hydroxides of Fe-Mn in contaminated soils leads to the absorption of Cu by Fe-Mn oxides. Absorption of Cu is done by Fe-Mn oxides, which is due to the co-precipitation of Cu in the Fe-Mn oxide network. OX fraction of Cu in 5% and 10% biochar treatments increased from 7.3% to 8% and 8.3%. Compared with the control treatment (Figure 4C), which is consistent with the results of the study of Jiang et al. [9], the OX fraction of Zn increased from 38.41% in the control treatment to 42% and 43% in the 5% and 10% treatments of CW biochar (Figure 5C). The average amount of Zn in the DC samples showed that most of the Zn were in the OX fraction, which is the most important factor controlling the behavior of Zn in the soil [12]. The reduction of the RES fraction of Zn in different treatments and its deformation into OX fraction can be one reason for the increase in Zn in the OX fraction. In comparison, it was observed that the OX fraction of Cu has a lower percentage than the remaining part.

Organic matter fraction

OM fraction of Cu showed the highest percentage of measured Cu in the control treatment (47%). This value

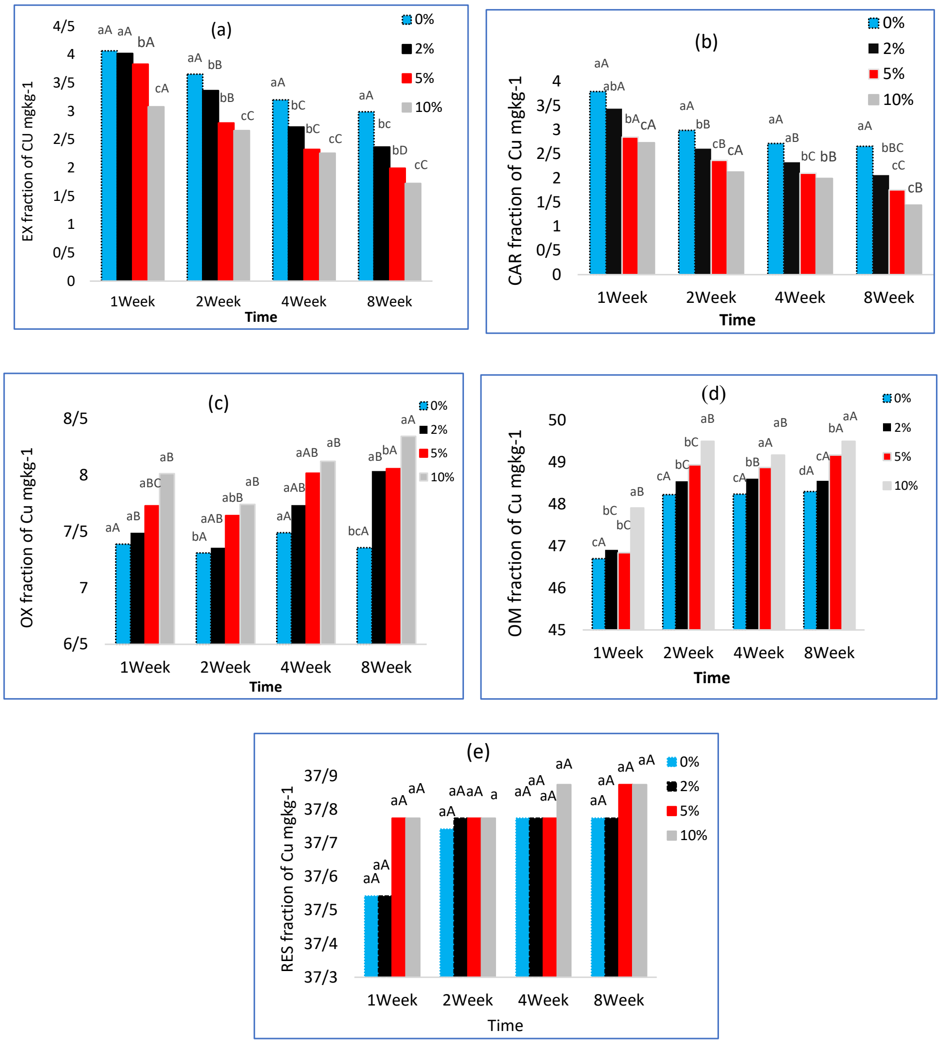

Figure 4. (a) The Exchangeable (EX) fraction, (b) Carbonate (CAR) fraction, (c) Oxides (OX) fraction, (d) Organic Matter (OM) fraction and (e) Residual (RES) fraction. Small letters indicate the effect of different CW biochar rates on chemical forms on Cu, and capital letters indicate the effect of biochar on different incubation times.

reached 50% after 10 weeks of incubation in 10% biochar treatment (Figure 4D). The high tendency of copper to organic compounds and creating a stable complex with organic functional groups at the biochar surface can increase Cu in OM fraction [35]. It is also important to note that Cu tends to bind to the organic matter in a complex form more than ion exchange [36]. Zn in the form of organic complex is significantly attached to OM fraction, and as a result, high absorption of Zn in the soil will control its mobility in the environment. The OM bind with Zn rises from 11.76% in the control sample to 16.49% in the 10% biochar treatment (Figure 5D). The OM fraction of Cu was higher than Zn (Figure 5D). Organic matter is selective towards ions, and the binding strength of metal ions with OM fraction decreases for Cu, Pb, Zn, and Ni, which may explain the low percentage of binding with organic matter Zn compared to Cu. Also, according to the results of this study, the OM fraction of Cu and Zn increases with the addition of biochar, which is similar to the results of the study of Mohammad et al. [20]. Increased SOC leads to acceleration in the formation of stable complexes attached to functional groups or organic compounds, which will increase the part attached to the organic matter in Cu and Zn [9, 10].

Residual fraction

The use of sequential capture methods showed that the RES fraction in Cu was greater than other fractions of the soil. The RES fraction of Cu increased from 37.54% in the control sample to 38% with 10% biochar treatment (Figure 4E). The high RES Cu fraction indicates that the

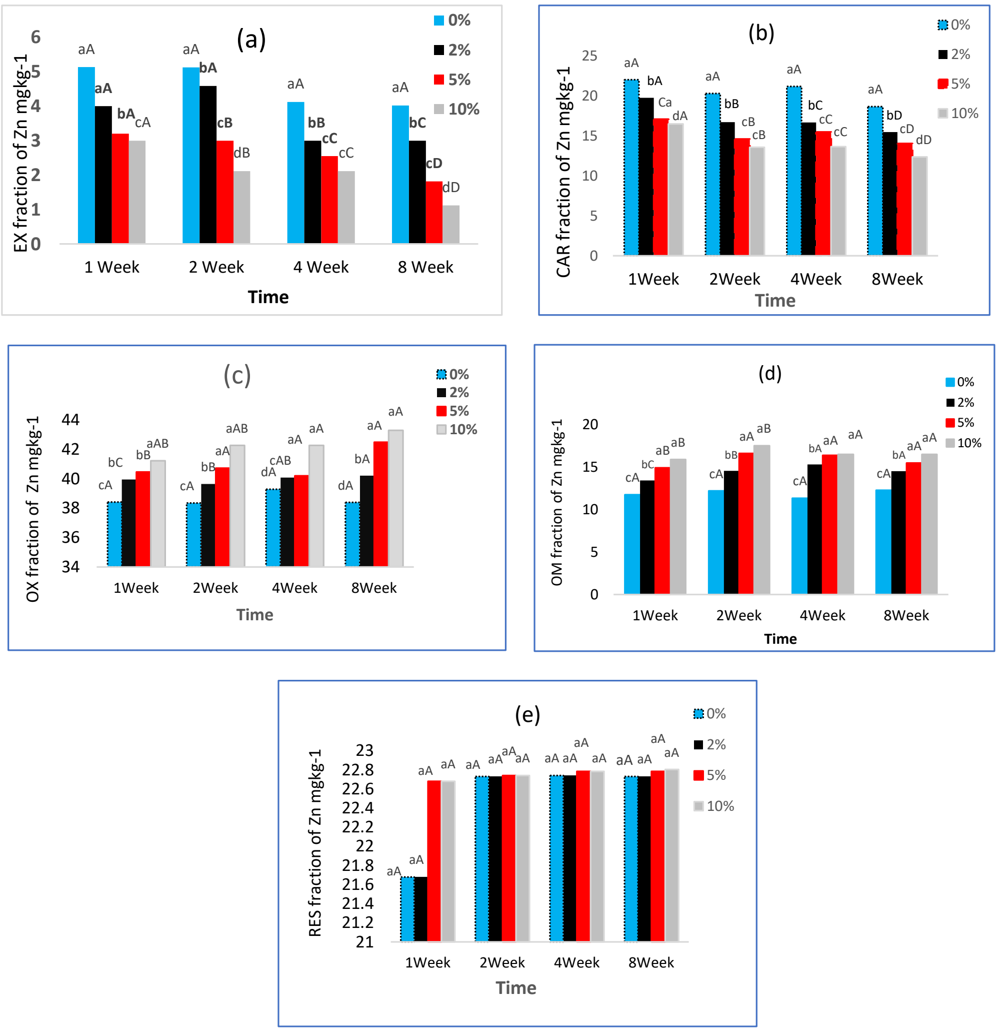

Figure 5. (a) Exchangeable (EX) fraction, (b) Carbonate (CAR) fraction, (c) Oxides (OX) fraction, (d) Organic Matter (OM) fraction and (e) Residual (RES) fraction. Small letters indicate the effect of different Conocarpus Waste (CW) biochar rates on chemical forms on Cu, and capital letters indicate the effect of biochar on different incubation times.

metal has little bioavailability in living organisms. A higher RES fraction of Zn from 21.68% in the control sample to 23% was observed in 10% biochar treatment (Figure 5E). Application of CW biochar in 10% treatment was more effective in increasing the RES fraction of Cu content than Zn. According to Chao et al. study, the application of peanut biochar reduces EX fraction of Zn and increases RES fraction of that in contaminated soil [33], which is consistent with the results of this study. There was also no significant difference between the amount of RES fraction of Zn and Cu in different biochar treatments. Biochar, by affecting soil properties, especially pH, changes the sequence of different sections of heavy metals in the soil and converts them to a stable form [34]. However, the use of biochar increased the amount of RES fraction of Cu compared to Zn. Similar to this study, an increase in the RES fraction of Cu in soil samples treated with biochar residues of apple pruning has been reported [35]. Besides, soil colloids can adsorb heavy metals in the form of ions and increase the RES fraction of heavy metals [36].

Distribution of chemical fractions

RES and OM fraction of Cu had the highest value in 10% biochar treatment. Besides, the distribution of chemical forms of Cu in the control sample was consistent with the pattern OM> RES> OX> EX> CAR, which is similar to the study conducted by Hamzenejad Taghlidabad et al. [35] (Figure 6A). The OX and RES fraction of Zn had the highest values. The divisions of chemical forms of Zn in the control sample were OX> RES> OM> CAR> EX, which in all treatments had the highest form of Zn related to OX and RES fraction (Fig-

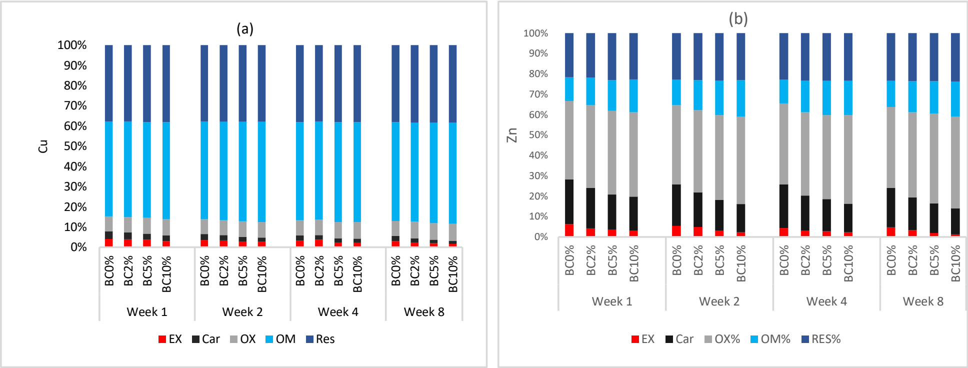

Figure 6. The chemical fraction of Cu (a), Zn (b) from sequential extraction in DC samples with different ratios of CW biochar at different incubation times

ure 6B). Hamidpour et al., in a study, showed similar proportions of chemical forms of Zn in contaminated soil [36]. Furthermore, the amount of OX fraction of Zn was higher than Cu, which is due to the higher adsorption of Zn on oxide surfaces.

4. Conclusion

The application of CW biochar in DC increases soil pH and improves soil quality, CEC, SOC, and EC, as well as reduces the mobility and bioavailability of Cu and Zn in DC. The Tessier sequential extraction method was showed that the EX fraction of Cu and Zn in 10% biochar treatment reduced by 2.34% and 4.13%, respectively, compared to the control. Furthermore, using the CW biochar at a rate of 10% had a greater effect on reducing the EX and CAR fraction of Cu and Zn and increasing the form OM and RES. According to the findings of this study, it was found that the use of CW biochar as an effective modifier can be reduced the bioavailability of Zn and Cu in DC.

Ethical Considerations

Compliance with ethical guidelines

There were no ethical considerations to be considered in this research.

Funding

This article was extracted from a PhD dissertation.

Authors' contributions

Conceptualization, Methodologys, Data analysis, and Writing – original draft: Zohre Lajmiri Orak, Sima Sabzalipour, Ebrahim Panahpour, Sina Attar Roshan, and Haman Tavakkoli; Investigation and Data collection: Sima Sabzalipour, Zohre Lajmiri Orak, Ebrahim Panahpour, and Haman Tavakkoli; Writing - review and editing: Ebrahim Panahpour; Reading and approval of the final manuscript: All authors.

Conflict of interest

The authors declared no conflict of interest.

Acknowledgments

The authors would like to express their sincere gratitude to the authorities of Ahvaz Islamic Azad University of Ahvaz Branch, Iran and National Iranian Drilling Company and Geology Department of Southern Oilfields (Karun).

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