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Reduction of Heavy Metal Movement in Soil Contaminated with Diesel Using Corncob-Biochar

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Abstract

This research aimed to study the effect of biochar on the stability of Mn, Cd, and Pb in soil contaminated with diesel. The clay with pH 6.80, medium in organic matter (OM), high in cation exchange capacity (CEC), low in phosphate and salinity was from Bang Rong Subdistrict, Klong Khuen District, Chachoengsao Province (N13˚50'32.1252" E101˚ 9'5.6808"). The metal content is in the standard for use in agriculture. The soil sample was prepared to contain Mn, Pb, and Cd at 2,000 mg/kg, 550 mg/kg, and 50 mg/kg, respectively. The biochar from corncob was neutral, low in CEC, high in conductivity and OM. The surface area, pore-volume, pore radius, acid neutralization capability, and the pH at the point of zero charges (pHPZC) were 61.189 sq. m/g, 0.088 mL/g, 13.664 Angstrom, 1,000 meq/kg, and 6.80, respectively. Five percent of biochar was mixed to the soil containing 2% and 5% of diesel at room temperature for 2, 4, and 8 weeks before extraction with diethylenetriaminepentaacetic acid (DTPA) and sequential extraction. The results indicated that the higher the amount of diesel in soil, the slower the metal movement. Biochar could retard the mobility of Mn, Pb, and Cd in the soil sample. Five percent of biochar was not enough to decrease the metal mobility in soil contaminated with diesel 5%. The amount of extracted heavy metals increased with the more extended mixing period. The addition of biochar to the soil sample could change metals from unstable to stable forms.

Keywords: Corncob-biochar; Diesel; Heavy metals; Mobility retardation; Soil

1. Introduction

The industry in Thailand is continuously developing, therefore, consuming a large number of petroleum products. According to the Ministry of Energy report (2017), Thailand produced crude oil 9,446 million liters and imported 49,675 million liters from abroad. The crude oil is sent to the refinery to convert to various fuel types for industrial plants and the general public. Data from the Department of Alternative Energy Development and Efficiency, Ministry of Energy states that Thailand used 1,645 million liters of gasoline, 4,263 million liters of diesel, 3,387 million liters of fuel oil, and 2,212 million liters of kerosene in 2017. Fuel oil, some diesel, and kerosene have been sent directly to the factory. Gasoline and some diesel have been sent to gas stations around the country. Department of Energy Business, Ministry of Energy reported that at the end of 2016, there were 25,343 gas stations in Thailand. Products are transported by land, except for fuel oil that is carried by water. Oil contamination in the environment is caused by spilling during transportation, leaking of underground oil wells at a gas station, or dumping contaminated oil waste to the environment at gas stations, garage, etc. At the same time, many industries release heavy metals to the environment, especially in industrial areas.

Industrial plants use heavy metals such as metal plating, batteries, electrical equipment, alloys, automobile parts. (Carolina *et al.,* 2017; Abdelhadia *et al.,* 2017). Many researchers indicated that plants grown in soil contaminated with heavy metals accumulated metals in different parts of the plant (Zhang *et al.,* 2010; Pinto *et al.,* 2015; Trebolazabala *et al.,* 2017). Metals were transmitted along the food chain and affected the health of humans who consumed contaminated food. Inorganic minerals (such as oxides, hydroxides, carbonates, phosphates, and fly ash) and organic components (such as biochar, food waste compost, and natural humic substances) are commonly added to soil to immobilize and stabilize heavy metals. The include direct mechanisms, such as adsorption, ion exchange, and precipitation. Many researchers studied the use of biochar to solve the problem of soil contamination with heavy metals. The biochar has a high porosity, a large number of negative ions on the surface; therefore, can absorb positive ions well (Jia *et al.,* 2017; Lahori *et al.,* 2017; Oliveira *et al.,* 2017; Tan *et al.,* 2017; Yin *et al.,* 2016; Poucke *et al.,*2018; Wang *et al.,* 2018). Corncob biochar was successfully used to immobilize Pb in soil (Rodriguez *et al.,* 2019). No researcher studied the case of soil contaminated with diesel and heavy metals. This research aimed to investigate the influence of diesel on biochar's efficiency in inhibiting the movement of heavy metals in soil. Corn is an essential economic crop in the country. In 2017, cultivating corn forage and corn for consumption throughout the country was 6.49 million rai and 2.34 million rai. The corn forage and corn for consumption yield were 5.07 million tons and 5.02 hundred thousand tons. (Office of Agricultural Economics, 2019). The discarded corncob should be used with benefit. The researcher intended to utilize the corncob by converting it to biochar and applying it to adsorb heavy metals in metals and diesel contaminated soil.

2. Materials and Methods

2.1 Sample Soil

The sample soil was topsoil (0-10 cm) from Bang Rong Subdistrict, Klong Khuen District, Chachoengsao Province. The site is located at N13˚50'32.1252" E101˚ 9'5.6808". After removing stones, debris, and grass, the soil was left to dry under the sun, ground with mortar, sieved with a 2 mm sieve (mesh no. 10), and dried in the oven at the temperature of 105˚C for 24 hours. The physical and chemical characteristics were determined using the method developed by the Department of Land Development (2014). Factors were as followed: soil texture (Hydrometer method), moisture (dry in an oven at 110ºC and calculating the mass loss.), pH (pH meter; Metrohm model 287), electrical conductivity (conductivity meter), cation exchange capacity (Ammonium acetate method), organic matter (Walkley–Black titrations), total nitrogen (Kjeldahl method), total phosphate (Molybdovanadophosphate method), and total heavy metals (EPA Method 3050B; Atomic absorption spectrophotometer; Perkin Elmer model AAS-200 New). The sample soil was spiked with $Mn(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, and $Cd(NO_3)_2 \cdot 4H_2O$ to achieve final Mn, Pb, and Cd concentration of 2,000 mg/kg, 550 mg/kg, and 50 mg/kg, respectively. The soil was left for one month at room temperature to allow spiked heavy metals equilibrium in soil.

2.2 Biochar

Corncob was washed with clean water, cut into small pieces, dried in the oven at 100°C for 24 hours, then passed through the pyrolysis process at 400°C for 4 hours. The biochar was crushed and then sieved through a 35mesh size. The biochar characteristics were determined using Scanning electron microscopy (SEM; Leo model 1455 VP), Fourier transform infrared spectroscopy (FTIR; Perkin Elmer model spectrum GX), X-ray diffraction spectroscopy (XRD; Bruker model D8 Advance), Brunauer-Emmett-Teller (BET) surface area analysis (Quantachrome model Autosorb iQ). The pH at the point of zero charges (pHPZC) was studied by adjusting a pH of 50 mL of

0.01 M NaCl to 2 - 12 using 0.01 M HCl or NaOH, adding 0.15g adsorbent, shaking at 120 rpm for 24 hours and then measuring the final pH (Rivera-Utrilla *et al.,* 2001). The acid neutralization capability (ANC) value was determined by the pH titration test (Venegas *et al.,* 2015). The determination of pH, electrical conductivity, cation exchange capacity, organic matter, total nitrogen, total phosphate, total metals were using the method developed by the Department of Land Development (2014).

2.3 Adsorption

The heavy metal contamination soil was prepared to contain 2% and 5% diesel. Biochar was then added at the ratio of 5%. The mixing soils were left at room temperature for 2, 4, and 8 weeks before extraction with 0.005 M diethylenetriaminepentaacetic acid (DTPA) (Zhang *et al.,* 2010). A six-step sequential extraction method was then carried out to investigate metals' forms in mixed soil samples (Tessier *et al.,* 1979). The metal in the soil sample was separated into six fractions by extracted with six types of the solution as follows: water (F1), 1 M magnesium chloride (F2), 1 M sodium acetate (F3), 0.04 M hydroxylamine hydrochloride in 25% acetic acid (F4), 0.02 M nitric acid, 30% hydrogen peroxide and 3.2 M ammonium acetate (F5), concentrated nitric acid (F6).

2.4 Statistical analysis

All samples were experimented in triplicate. A standard deviation was observed to identify the precision of the experiment. The average was used to critique the results. Two-way analysis of variance (ANOVA) using MINITAB version 16 was carried out to test the data difference within and between the experimental set at 95% confidence level.

3. Results and discussion

3.1 Soil and biochar characteristics

Table 1 showed the characteristics of the sample soil. The soil collected from Bang Rong Subdistrict, Klong Khuen District, Chachoengsao Province, contained 43.58% sand, 5.71% silk, and 50.71% clay. According to the soil texture triangle defined by the United States Department of Agriculture, the sample soil was clay. The results corresponded to the Department of Agriculture database, which states that the soil from Khlong Khuen District, Chachoengsao was clay and classified in the third set soil (Department of Agriculture, 2012). The soil was slightly acid with a pH of 6.80, high moisture content due to poor drainage. The salinity level was within the low standard range (0 - 2 dS/m).

Table 1. Soil and biochar characteristics

Parameters	Soil	Biochar
Particle distribution		
Sand (%)	43.58 ± 1.51	-
Silt (%)	5.71 ± 0.72	-
Clay (%)	50.71 ± 2.00	-
Soil type	clay	-
Electrical conductivity (dS/m)	0.002 ± 0.000	11.15 ± 0.10
Organic matter (%)	2.60 ± 0.10	6.63 ± 0.27
Total phosphate (mg/kg)	0.06 ± 0.01	0.08 ± 0.03
Moisture (%)	14.93 ± 0.55	-
pH	6.80 ± 0.01	7.15 ± 0.21
CEC (cmol/kg)	22.18 ± 0.41	10.96 ± 0.02
Total N (%)	16.33 ± 4.04	13.94 ± 0.06
Cd (mg/kg)	17.90 ± 0.03	Nd
Pb (mg/kg)	41.50 ± 0.01	13.04 ± 1.23
Mn (mg/kg)	175.88 ± 0.06	27.03 ± 3.04

Nd = non detected

The value of CEC, OM, and total nitrogen was within the high standard range of 20 - 30 cmol/kg, 2.5 - 3.5%, and > 15%, respectively. The studied soil was clay with high CEC and OM values, indicating a high adsorption site. Under soil standards for use in housing and agriculture, the soil must have the concentration of Mn, Cd, and Pb not more than 1,800 mg/kg, 37 mg/kg, and 400 mg/kg, respectively (Announcement of the National Environment Board No. 25, 2004). The concentration of three metals in the soil sample did not exceed the standard value.

The characteristics of biochar were presented in Table 1. Biochar was slightly alkaline, with a pH of 7.15. The salinity and OM values were in the high-level range, 8 - 16 dS/m and > 4.5%. The CEC and total nitrogen values were in the medium-level range, 10 - 15 cmol/kg and 10 - 14%. The level of total phosphate was low (0.01 - 0.1 mg/kg). Adding biochar to the soil could increase the pH, OM, and CEC of the soil, which can positively affect the ability to absorb metals. Cadmium and lead levels in biochar were below the maximum allowed thresholds of the International Biochar Initiative (IBI) (Initiative, 2015). Manganese level is not defined the maximum allowed thresholds. The range of maximum allowed thresholds was 1.4 - 39 mg/kg for Cd and 121 - 300 mg/kg for Pb.

The image from the scanning electron microscope showed the porous surface of biochar with variable hole sizes (Figure 1). Data from Brunauer-Emmett-Teller (BET) surface area analyzer demonstrated that the biochar surface area, pore-volume, and pore radius were 61.189 m^2/g, 0.088 ml/g, and 13.664 Å, respectively. The surface area of corncob-biochar (pyrolysis at 600˚C) studied by a previous researcher was 183 m^2/g (Budai *et al.,* 2014). The surface area of the biochar in this study was lower due to a lower pyrolysis temperature.

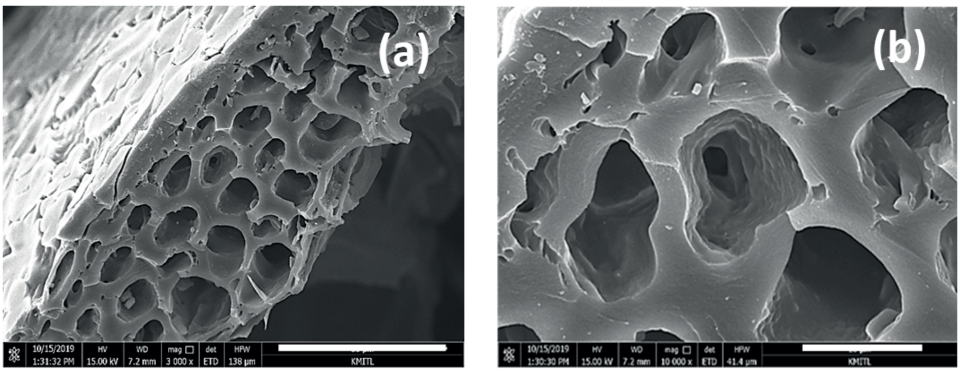


Figure 1. The image from the scanning electron microscope of corncob-biochar (pyrolysis at 400°C) (a) mag 3,000x (b) mag 10,000x

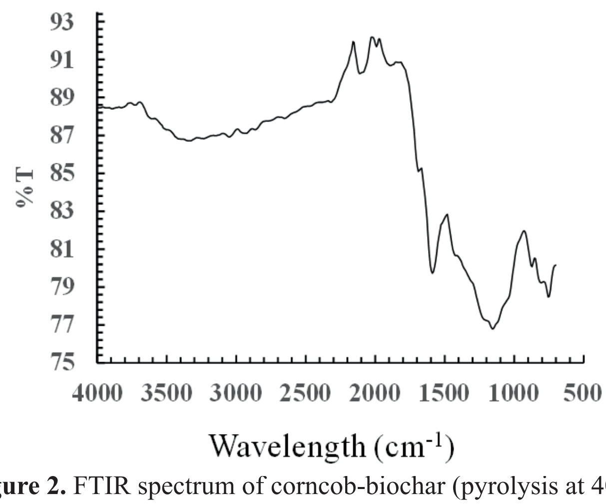


Figure 2. FTIR spectrum of corncob-biochar (pyrolysis at 400°C)

Figure 2 showed the FTIR spectrum. The band at 3,334.81 cm^{-1} (O - H stretching due to phenols, alcohols, and carboxylic acids), 1,592.98 cm^{-1} (-C = C stretching, aromatic rings present in lignin), and 1,034.60 cm^{-1} (C - O stretching) indicated the presenting of cellulose, hemicellulose, and lignin due to a low pyrolysis temperature (400˚C). The cellulose, hemicellulose, and lignin content in corncob before pyrolysis were 37.15%, 40.73%, and 7.22%, respectively. After pyrolysis at 480˚C, the content was as followed: cellulose (non-detected), hemicellulose (2.69%), and lignin (89.36%) (Srilek and Aggarangsi, 2019). During pyrolysis, the moisture evaporation causes breakage of bonds and formation – COOH and –CO groups (Ca´rdenas-Aguiar *et al.,* 2017). Pyrolysis below 500˚C, cellulose and hemicellulose decomposed at a fast rate. A higher temperature is required to degrade lignin. The functional groups in cellulose, hemicellulose, and lignin can play an important role in the adsorption of metals.

The pH titration test showed that the acid neutralization capability value (ANC) of corncob-biochar was 1,000 meq/kg. From the previous study, the values of ANC of biochar produced from durian and mangosteen shell were 1,464.80 meg/kg and 1,328.98 meq/kg, respectively (Chaiyaraksa *et al.,* 2017). The ANC value of corncob-biochar was lower than the biochar from durian and mangosteen due to the lower pH of corncob-biochar. Venegas explained that adding the material with high ANC value to the soil can raise the soil pH (Venegas *et al.,* 2015). The pH at which the total biochar surface's net charge equal to zero (pHPZC) was 6.00. Biochar can absorb metals well when added to soil with a pH value > 6.00. The soil pH in this study was 6.80, so biochar showed good metal adsorption efficiency.

3.2 Extraction with DTPA

DTPA can extract metals in soluble, exchangeable, and some of the organically bound fractions. Considering the heavy metal contaminated soil (S) and heavy metal contaminated soil mixed with 5% biochar (S + B), it showed that biochar caused the heavy metals to be less extracted (Figure 4). Heavy metals can adsorb on biochar through both chemical and physical mechanisms. Biochar from corncobs has a pore volume of 0.088 ml/g, which heavy metals can enter the pores and be captured by a physical mechanism. For chemical mechanisms, the possibilities are as in Figure 3. Heavy metals can adsorb on the biochar by ion exchange, metal extraction, and precipitation mechanism (Li *et al.,* 2017). The interchanging between heavy metal ions in the soil solution and cations can occur at the biochar surface. Carboxyl, alkoxyl, hydroxyl groups can release protons, becoming negatively charged, leading to electrostatic attraction with heavy metal ions. Formation of metal precipitates with inorganic constituents and coordination of metal ions with π electrons (C = C) of biochar is possible.

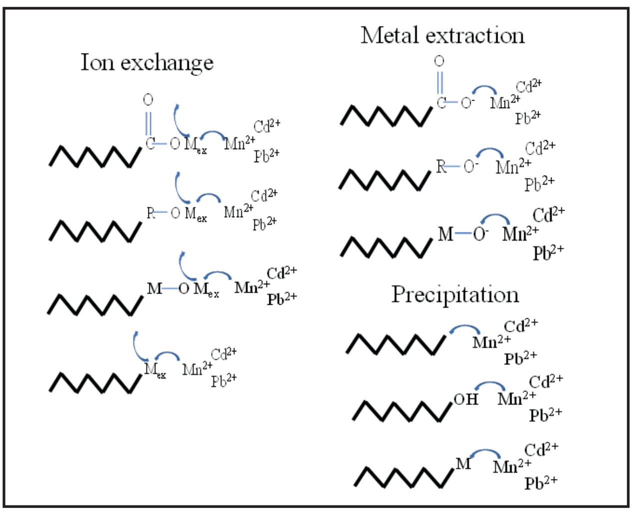


Figure 3. Chemical adsorption mechanism on biochar

Experimenting on soil with diesel (2% and 5%) and without diesel, results showed that diesel in the soil reduced heavy metals extraction by DTPA (Figure 4). At two weeks of adding biochar to the soil, metals' mobility decreased 5 - 8% when there is no diesel in the soil and 10 - 16% when there is diesel in the soil. For eight weeks, biochar affected mobility by 2 - 6% when there is no diesel in the soil and 0 - 9% when there is diesel in the soil. By comparing S + 2% D and S + 5% D samples, heavy metals were extracted less when 5% diesel was present in the soil. The reason may be the heavy metal changed from an unstable form to the form bound to organic matter, which is a stable form.

The extracts from S + 5%D and S + 5% D + B were not significantly different at 95% confidence level tested by Two-way ANOVA. The addition of 5% of biochar was not enough to stabilize heavy metals in the soil containing 5% diesel.

When comparing the extraction of samples left in the period of 2, 4, and 8 weeks, it indicated that the longer the leaving period, the higher the extracted metals. The possibility was that some diesel evaporated and decomposed when leaving for an extended period.

DTPA could extract Mn the most because manganese concentration was the highest, so the adsorption site was not enough to adsorb Mn ion tightly. On the other hand, the concentration of cadmium in soil was the lowest. Cadmium was the least extracted.

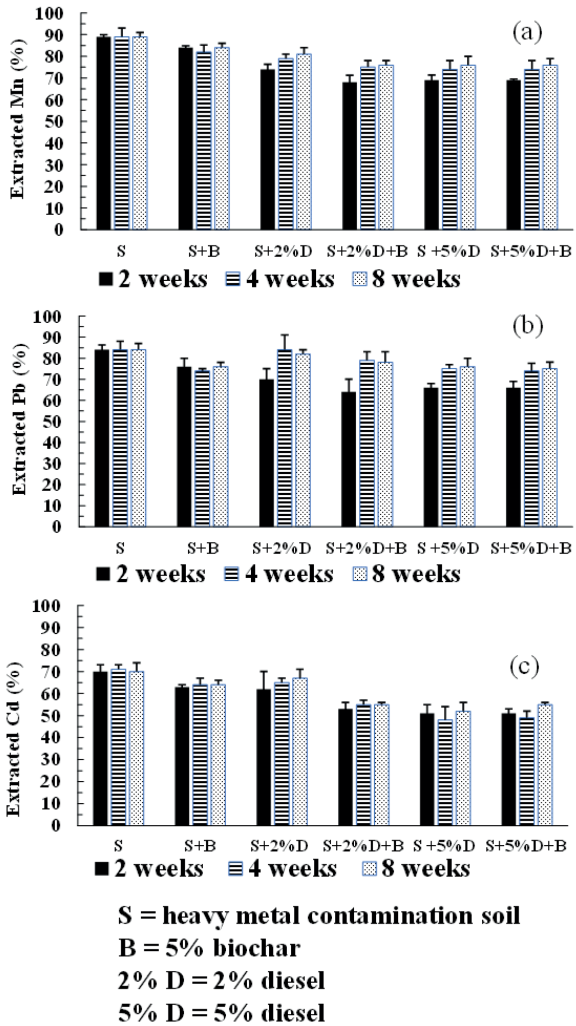
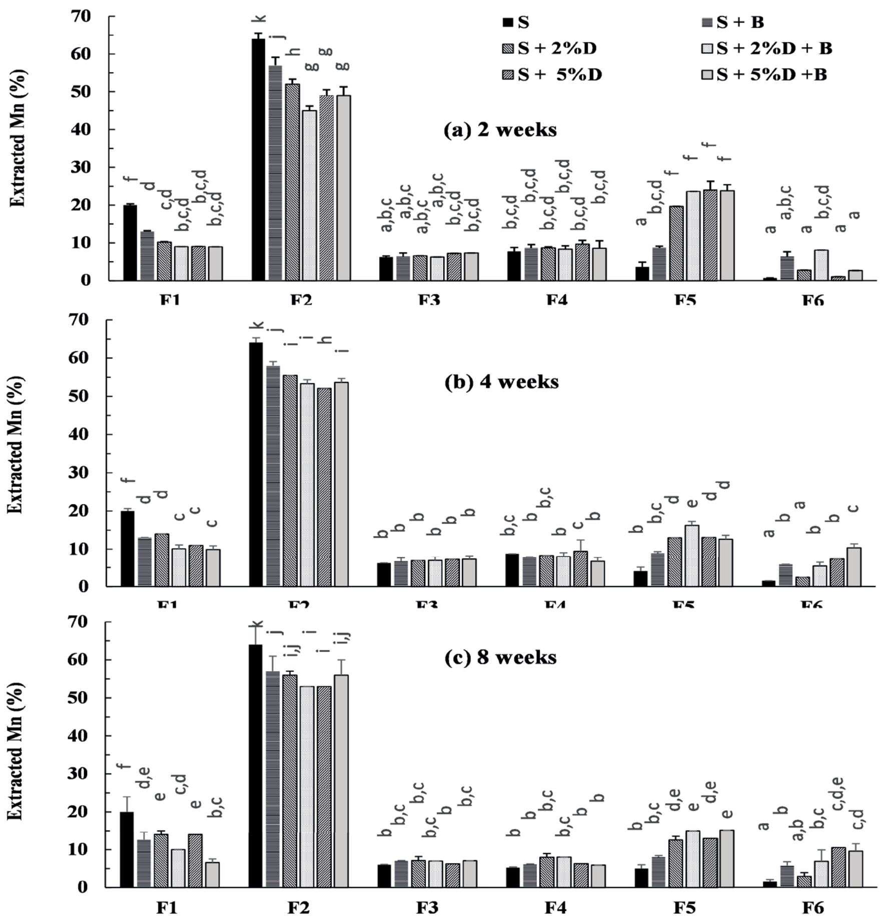


Figure 4. Percent of extracted metals (a) Mn (b) Pb (c) Cd by DTPA after 2, 4, and 8 weeks incubation time

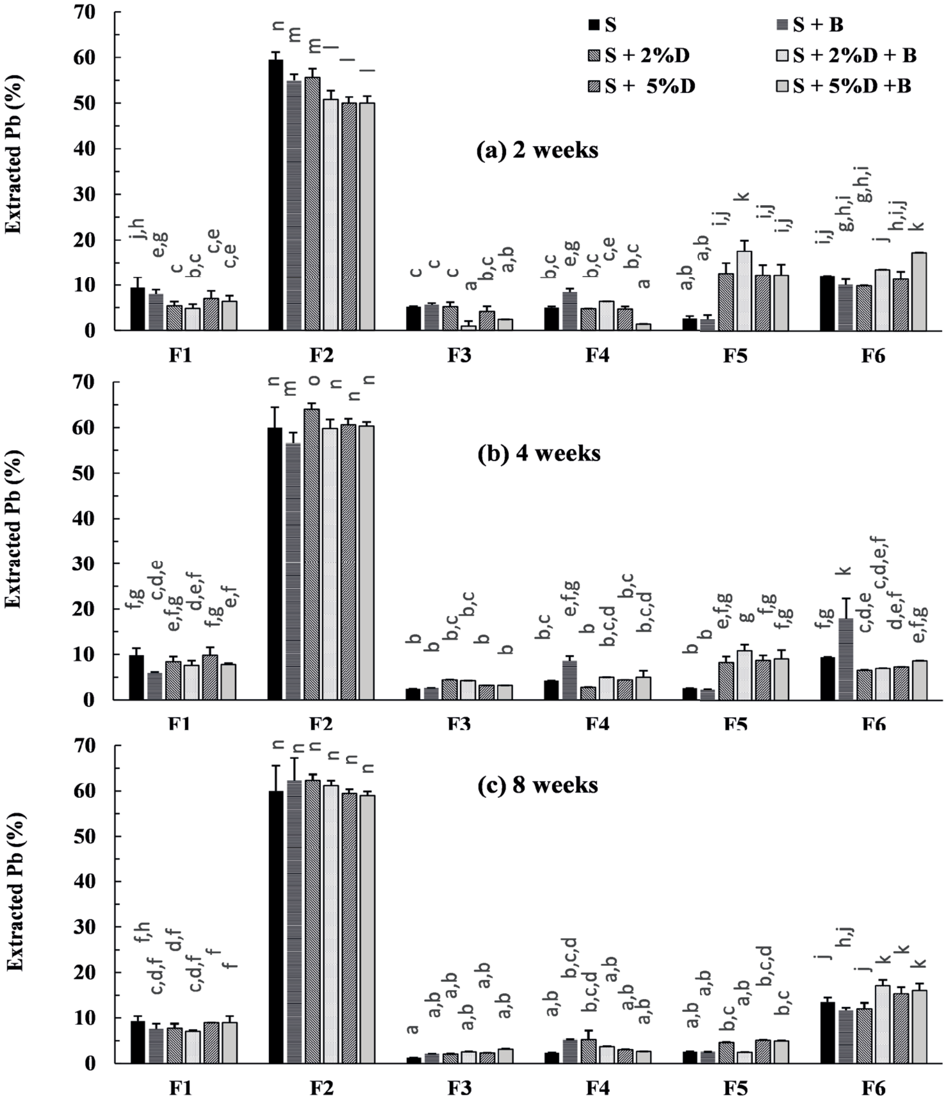
3.3 Sequential extraction

Six steps sequential extraction is a defined method commonly used to determine six geochemical forms of metals bounded to different soil solid phases. The six forms are water-soluble form (F1), exchangeable form (F2), carbonate bound form (F3), Fe-Mn oxide bound form (F4), organically bound form (F5), and residual form (F6). The first three forms (F1, F2, and F3) are unstable in the environment. Metals in the unstable form can move in the environment easier than the other forms (F4, F5, and F6). The soluble and exchangeable fractions are readily bioavailable and acid extractable fractions. The Fe-Mn oxide bound and organically bound fractions are a reducible and oxidizable fraction, respectively, whereas the residual fraction (bound within the crystal lattices of the rocks and minerals) is not available for plants in the long term (Malandrino *et al.,* 2011; Lu *et al.,* 2017; Fernández-Ondoño *et al.,* 2017).



Note: The character a, b, c, d, e, f, g, h, i, j and k mean the statistically significant difference ($p < 0.05$). The different character represents a significant difference. The same character represents a non-significant difference.

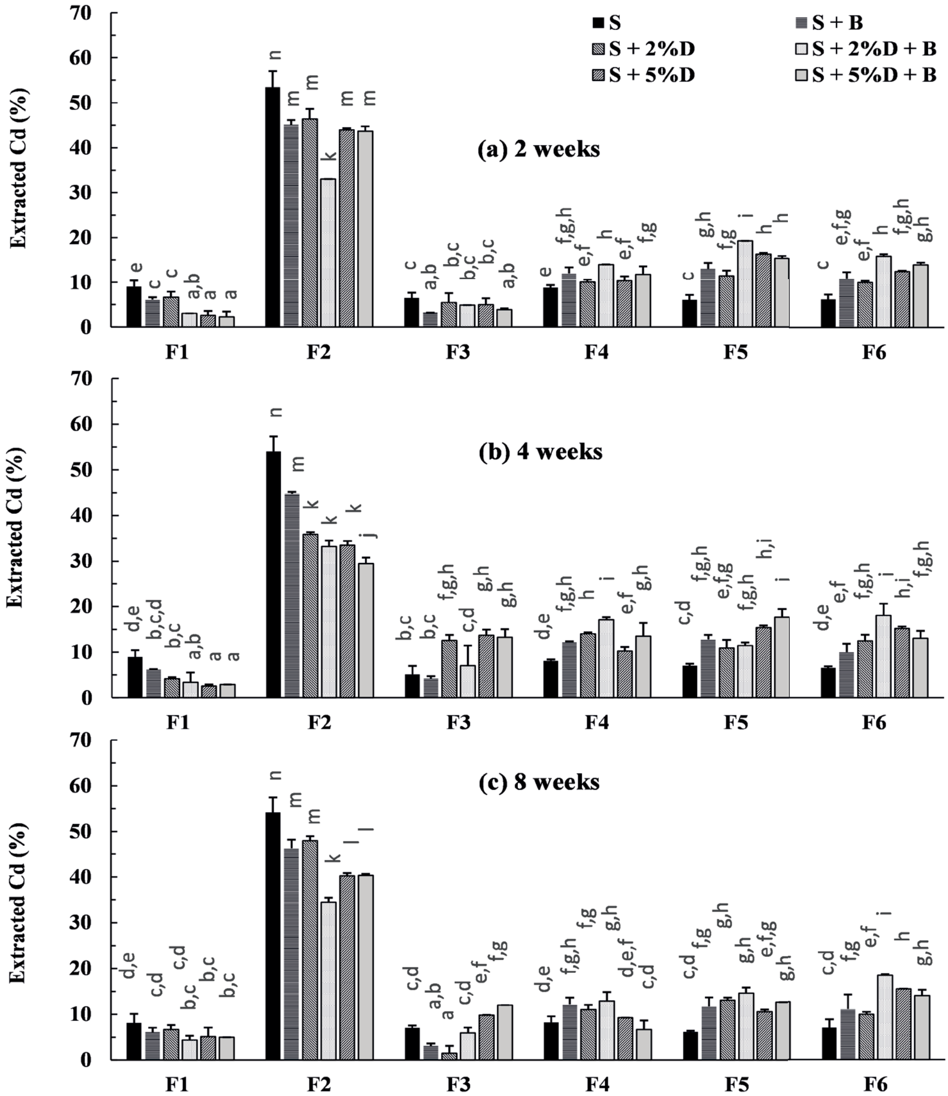
Figure 5. Percent of six forms of Mn extracted from the soil after various incubation time (a) 2 weeks (b) 4 weeks (c) 8 weeks



Note: The character a, b, c, d, e, f, g, h, i, j, k, l, m, n and o mean the statistically significant difference (p <0.05). The different character represents a significant difference. The same character represents a non-significant difference.

Figure 6. Percent of six forms of Pb extracted from the soil after various incubation time (a) 2 weeks (b) 4 weeks (c) 8 weeks

Figure 5 to Figure 7 showed that heavy metals were mainly in the exchangeable form (F2). This result was consistent with the soil properties mentioned in Section 3.1. The studied soil was clay with high CEC value. Metals in an organically bound form (F5) increased when adding biochar because biochar contained cellulose, hemicellulose, and lignin. Metals changed from an unstable form to a stable form when diesel was presented in the soil. Comparing between two weeks, four weeks, and eight weeks, the longer the incubation time, the lower the metals in an organically bound form. Diesel may be partially evaporated and decomposed when leaving an extended period. The unstable form of Mn was higher than the Cd and Pb. The results from sequential extraction were correlated to DTPA extraction.



Note: The character a, b, c, d, e, f, g, h, i, j, k, l, m and n mean the statistically significant difference ($p < 0.05$). The different character represents a significant difference. The same character represents a non-significant difference.

Figure 7. Percent of six forms of Cd extracted from the soil after various incubation time (a) 2 weeks (b) 4 weeks (c) 8 weeks

4. Conclusions

Biochar could reduce Mn, Pb, and Cd movement in the soil. The presence of diesel in the soil increased the organic matter, thus slowing down the heavy metals' movement. The mobility of Mn, Cd, Pb decreased 7%, 10%, 17% when adding 5% biochar to the soil without diesel, and 16%, 12%, 10% when there were 2% diesel in the soil. As diesel content increases, heavy metals move less in soil. Curing heavy metals in the soil for two weeks resulted in less heavy metal movement than curing for eight weeks. As a result of sequential extraction, the heavy metal changes to a more stable form when adding biochar to the soil. The other factors affecting heavy metals' movement are metals' concentration in soil and length of time.

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