



RESEARCH ARTICLE

ASSESSING THE EFFECT OF BIOCHAR ON ADSORPTION EFFICIENCY OF HEAVY METALS IN CONTAMINATED SOIL SOLUTION

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ABSTRACT

Environmental contamination by heavy metals has become a world-wide problem during recent years, due to the fact that heavy metals, unlike some other pollutants are not biodegradable. The potential of maize-cob derived biochar on the adsorption of heavy metals (Cu, Pb, Zn and Cd) as a remedy to soil pollution was evaluated in this study. Soil samples were collected randomly from vegetable gardens around Jaba in Kano, Kano State. Soil samples were digested using a mixture of HF- HNO₃-HCl in order to determine the heavy metal content by Atomic Absorption Spectrophotometer AAS. Equilibrium experiments were carried out on the effects of various parameters like initial concentration, dosage of adsorbent and shaking time on a batch adsorption system as different doses of maize-cob derived biochar (0.2g, 0.4g and 0.6g) and were incubated with varying concentration of Cu, Pb, Zn (50mgL⁻¹, 100 mgL⁻¹, and 200 mgL⁻¹) and Cd (5 mgL⁻¹, 10 mgL⁻¹ and 20 mgL⁻¹) for 3 days. Concentrations of metals were determined after shaking time of 2 hour, 4 hour and 6 hour using AAS. Adsorption increased with increase in initial concentration for Pb, Zn and Cd as their best sorption percentages were observed at 200 mgkg⁻¹ while, Cu had its best sorption at lower concentrations. Increasing the biochar dose across all the metals tested did not cause any significant change in percentage removal of metal ion, however, a specific trend was observed; shaking time across all the metal under test as equilibrium adsorption were attained within 2 hours. Adsorption Coefficient depended strongly on initial concentration and up to 96% of all the target metals were achieved. This study shows that maize-cob derived biochar is a promising inexpensive adsorbent for metal ion removal from aqueous solutions in soil.

KEYWORDS

Biochar, adsorption efficiency, heavy metals, contaminated soil.

1. INTRODUCTION

Heavy metals are a group of metallic elements characterized by their high density (3.5 - 7gcm⁻³) and potential toxicity, even at low concentration (Inobeme et al., 2014). These elements can cause harm or poisoning if ingested, inhaled, or exposed to in small amount. They display distinct chemical characteristics including multiple oxidation states, paramagnetism and vibrant colored complexes. They exist in different forms and are associated with a range of soil components which determines their bioavailability and reactivity (Tack et al., 2006). Heavy metals are released into the environment through man's industrial, domestic and commercial activities (Ukpong et al., 2013). The major natural source of heavy metal contamination in soil is by pedogenesis. Heavy metals are considered one of the major sources of soil pollution. In excessive concentration, heavy metals such as Cd, Cr, Cu, Hg, As, Ni, Pb and Zn are regarded as the most toxic and environmentally damaging. However, some of these heavy metals, especially those that are transition metals, are also essential for plant metabolism (e.g. Cu, Ni, and Zn) (Ross, 1994). In arid and semi-arid regions, the escalating demand for water, driven by industrial expansion and population growth, has outpaced the available natural freshwater resources, prompting the exploration and adoption of innovative alternative irrigation water sources to bridge the gap and ensure sustainable water management. (Hassanli et al., 2009). Irrigation water from alternative sources may harbor high concentrations of salts, toxic ions, heavy metals, and organic residues, which can

accumulate in soil and pose a dual threat: compromising agricultural productivity and contaminating the food chain, thereby endangering both the environment and human health (Jahantigh, 2008). Among various strategies explored for mitigating metal pollution, adsorption has emerged as a standout approach, offering a compelling blend of efficacy, safety, and affordability. As a straightforward, non-intrusive, and cost-effective method, adsorption has proven particularly well-suited for removing heavy metals from industrial effluents, making it a promising solution for environmental remediation. (Shah et al., 2009; Rahmani et al., 2009). The term "adsorption" is a process where a substance is attracted and bound to the surface of a solid material, transitioning from a liquid state to a solid-attached state through physical and/or chemical forces, resulting in a concentrated accumulation of the substance on the solid's surface (Babel and Kurniawan, 2003). The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment. A number of studies have focused on the removal of heavy metals with cheaper and locally available adsorbents to replace cost intensive heavy metal removal methods from contaminated soils and water (Quek, 1998; Babarinde, Oyebamiji and Adebowale, 2006; Hanafiah, Shafiei, Harun and Yahya, 2006; Pingxiao et al., 2011). Biochar has gained an acceptance in this regard and is increasingly being evaluated. Biochar, a carbon-rich solid derived from the pyrolysis of agricultural waste biomass in low-oxygen conditions, has emerged as a promising solution for soil remediation. Its exceptional properties, including a vast internal surface

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area, negative charge, and durability, make biochar an ideal candidate for effectively mitigating contaminated soils and restoring ecosystem health (Mukherjee et al., 2011).

The global surge in environmental contamination by heavy metals poses a significant threat, as these pollutants persist indefinitely due to their non-biodegradable nature. In Nigeria, inadequate environmental regulations and enforcement exacerbate the issue, leading to the widespread use of untreated domestic sewage and industrial effluent for irrigation, contaminating crops and vegetables with heavy metals, and highlighting the urgent need for effective wastewater management strategies (Khan et al., 2008; Olayiwola and Bernard, 2016; Bayero et al., 2018). The use of wastewater for irrigation can significantly contribute to the increase of heavy metals content in the soil and food chain (Ullah et al., 2012; Hussain et al., 2013). Accumulation of pollutants in soil poses a significant threat to agricultural productivity and environmental sustainability, necessitating effective remediation strategies. A range of methods exist for remediating metal-polluted soils, including physical, chemical, and biological approaches. While techniques like ion exchange, chemical precipitation, and microbiological precipitation have been developed to extract heavy metals from water, their widespread adoption is hindered by high capital, labor, and energy requirements, underscoring the need for more efficient and sustainable solutions. Recently, biochar has been proposed as a cost-effective amendment for metal immobilization in soils (Beesley et al., 2011). Maize cobs are agricultural residues that are abundant and mostly used as fuel. The use of maize cob derived biochar for remediation may not only be cost effective but environmentally friendly. This study was aimed at assessing the effect of biochar on adsorption efficiency of heavy metals in contaminated soil solution.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

2.1.1 Soil Sampling

Soil samples were collected at a depth of 0–20 cm, where most of the rooting activities of vegetables occurred. Samples were collected randomly from 2 farms of less than 0.1 ha in size. In each farm five soil samples were collected. All samples from the farm were bulked together to obtain a composite sample which was divided into three samples. The samples were air-dried, crushed gently with mortar and pestle, and was then sieved through a 2 mm sieve mesh. Soil was sampled from vegetable farms in Jaba, along the Jakara river of Fagge Local Government Area of Kano State.

2.2 Preparation of Biochar

Maize cobs for biochar production were collected from Bayero University, Kano farm. The maize cobs were sun dried for 72 hours to moisture content of < 10% and crushed. The biochar was produced by heating the maize cob at 400°C for 3 hours in a fabricated pyrolysis kiln based on the recommendation of Lehmann (2007). The kiln consisted of an airtight cylindrical metal drum and butane combustion burners. After the pyrolysis process, the biochar was allowed to cool overnight before grounding to small granules and pass through 2mm sieve in order to have the same particle size as that of the soil.

2.3 Laboratory Analysis

2.3.1 Soil Analyses

Samples collected from the field were subjected to laboratory analyses using the following established procedures. All analyses were replicated three times. The pH was determined using the 1:2.5 soil-water ratio using EL model 720 pH meter; particle size analysis was done using the hydrometer method as outlined in (Adepetu et al., 2000). The EC of the samples was determined using 1:2.5 soil-water ratio used in pH determination with EC meter, Janway, 4520 model.

The bulk density of the soil was determined using the core samples method as outlined in (Jaiswal, 2004). Fresh weight of the core sample was taken before placement into an oven where it was oven dried to constant weight at 105°C for 24 hours. The Walkley-Black wet oxidation method as outlined in (Adepetu et al., 2000) was used to determine the organic carbon content of the soil. The soil available phosphorus was extracted using Bray 1 method (Bray and Kurtz, 1945) because of the slightly acidic nature of the soils under investigation, and determined using the Blue method (Drummond and Maher, 1995). The neutral ammonium acetate extraction technique (Jaiswal, 2004) was used in extracting the bases.

Sodium and potassium was determined by flame emission, using an EEL Flame Photometer while Calcium and Magnesium were determined using Atomic Absorption Spectrophotometer (Agilent 200 Series, 240 FS)

The exchangeable acidity was determined by the Peech method; the total nitrogen was determined using the micro-Kjeldahl Method as outlined by Jaiswal in 2004. Digestion tubes were soaked in 1M HCl for 24 hours before digestion and 1 g of each soil fraction was weighed and placed into the presoaked digestion tubes. A mixture of HF-HNO₃-HCl in ratio of 2: 6: 1 was prepared and 9 ml of the mixture was added to each sample and digested for 2 hours. After 2 hours, the samples were allowed to cool to room temperature, then filtered and diluted to 50 ml with distilled water. Total amount of Cu, Cd, Pb and Zn present in the solution was determined using the AAS

2.3.2 Determination of Total Heavy Metals in Biochar

The total content of Cu, Cd, Zn, and Pb in the biochar was determined by digestion of the biochar with a mixture of HCl-HNO₃ following the procedure outlined by Lim and Jackson IN 1986. After digestion, the suspension was filtered through Whatman No. 42 filter paper into a 100 ml volumetric flask and total concentration of Cu, Cd, Zn, and Pb in the biochar was determined using the Atomic Absorption Spectrophotometer (AAS).

2.4 Batch Experiment

2.4.1 Soil Incubation

Each of the soil fractions was mixed thoroughly with the biochar in the ratio of 5:1, 2.5:1 and 1.6:1 (i.e. 1 g of soil: 0.2g of biochar, 1 g of soil: 0.4g of biochar and 1 g of soil: 0.6g of biochar).

The soil sample plus biochar was transferred into the incubation vessels and 25 mls each of the varying concentrations of heavy metal (50 mgkg⁻¹, 100 mgkg⁻¹ and 200 mgkg⁻¹ for Cu, Pb and Zn, and 5 mgkg⁻¹, 10 mgkg⁻¹, 20 mgkg⁻¹ for Cd per gram of soil) was added and the samples left for the desired incubation period of 3 days.

After the incubation period and moisture content of 75%, the samples were placed on mechanical shaker and shaken for a period of 2, 4 and 6 hours. Twenty (20) ml of the suspension was taken and filtered into a bottle after each shaking period and the amount of Cd, Cu, Pb and Zn left in the suspension was determined using the AAS. The amount sorbed by the soil was calculated as:

$$\text{Amount sorbed by soil} = \frac{\text{initial concentration of the solution} - \text{final concentration}}{\text{Initial concentration} \times 100} \quad (1)$$

2.4.2 Data Analysis

Data were subjected to analysis of variance (ANOVA) using Genstat (Genstat, 17th edition)

The adsorption efficiency of each biochar was determined by

$$\frac{C_e - C_t}{C_e} \times 100 \quad (2)$$

Where C_e = concentration at equilibrium

C_t = concentration at time t

3. RESULTS

3.1 Physical and Chemical Properties of Soil and Biochar

Table 1 shows the initial condition of the soil. The soil has a mean of 20.45% soil moisture content, and a medium to high soil bulk density of 1.62g/cm³. The pH indicates that the soil is slightly acidic. However, low organic carbon of 0.881% was observed. 73.01% of sand, 19.33% of silt, 7.65% clay was also observed, indicating loamy sand soil texture. The total heavy metal content of the soil; Cu, Pb, Zn and Cd were found to be 0.06 mgkg⁻¹, 0.0532 mgkg⁻¹, 0.7472 mgkg⁻¹, and 0.0557 mgkg⁻¹ respectively.

On the other hand, the soil moisture content (SMC) of biochar was very low (1.01%), While 7.72 was observed as the pH in water indicating that it was slightly alkaline, a high organic carbon content of 65.2% was recorded, The total heavy metal content of were generally low; Cu, Pb, Zn and Cd in biochar was found to be 0.017 mgkg⁻¹, 0.017 mgkg⁻¹, 0.360 mgkg⁻¹, and 0.025 mgkg⁻¹ respectively.

Table 1: Physical and chemical properties of the experimental soil and biochar.

Soil properties	Soil	Biochar
SMC (%)	20.45	1.01
Bulk density (g/cm ³)	1.62	-
pH in H ₂ O	6.913	7.72
pH in KCl	6.093	-
E.C (dS/m)	0.198	0.62
E. A (cmol/kg)	1.667	0.51
ECEC (cmol/kg)	7.778	7.18
OC (%)	0.881	65.6
%O.M	1.399	-
%Sand	73.01	-
%Silt	19.33	-
%Clay	7.653	-
Textural class	Loamy sand	-
TN (g/kg)	0.7	10.1
Av.P (mg/kg)	9.623	33.06
K (cmol/kg)	0.499	3.81
Cu (mgkg ⁻¹)	0.06	0.017
Pb (mgkg ⁻¹)	0.0532	0.017
Zn (mgkg ⁻¹)	0.7472	0.360
Cd (mgkg ⁻¹)	0.0557	0.025

SMC = Soil Moisture Content, EC = Electrical Conductivity, TN = Total Nitrogen, Av.P = Available Phosphorus, EA = Exchangeable acidity, OC = Organic Carbon, ECEC = Exchangeable Cation Exchange Capacity, K = Potassium.

3.2 Sorption Equilibrium Study

3.2.1 Adsorption efficiency of Cu, Pb, Zn and Cd by different doses of biochar at different shaking times

The adsorption efficiency of the different doses of biochar at different shaking time for the different metals is presented in Table 2. A significant

difference ($p < 0.05$) was observed in the sorption of Cu (98.32%) when 200 mgkg⁻¹ was used as compared to 100 mgkg⁻¹ (99.70%) and 50 mgkg⁻¹ (98.85%). At a concentration of 200 mgkg⁻¹, amount of Pb adsorbed (99.89%) was statistically similar to that of 100 mgkg⁻¹ (99.90%) but showed a difference at the concentration of 50 mgkg⁻¹ (99.80%). Zn showed a significant difference ($p < 0.05$) between the different concentration (50 mgkg⁻¹, 100mgkg⁻¹ and 200 mgkg⁻¹) and sorption increased with concentration (97.74%, 99.00% and 99.42%) respectively. Similarly, a significant difference ($p < 0.05$) was observed in the sorption of Cd between the different concentrations (5mgkg⁻¹, 10mgkg⁻¹ and 20mgkg⁻¹) and sorption percentages were (98.47%, 97.26% and 99.02%) respectively.

Table 2: The adsorption efficiency percentage of Cu, Pb, Zn and Cd ion by different doses of biochar at different shaking times

Treatment	Cu	Pb	Zn	Cd
		%		
Concentration (mgkg ⁻¹)				
0	0	0	0	0
50 (5)	99.85 ^a	99.80 ^b	97.74 ^c	98.47 ^b
100 (10)	99.70 ^a	99.90 ^a	99.00 ^b	97.26 ^c
200 (20)	98.32 ^b	99.89 ^a	99.42 ^a	99.02 ^a
SE ±	0.0655	0.0154	0.0173	0.1113
Biochar (g)				
0.2	99.28	99.86	98.80	98.25
0.4	99.30	99.87	98.76	98.30
0.6	99.27	99.85	98.81	98.19
SE ±	0.1498	0.0179	0.1236	0.182
Shaking Time (hours)				
2	99.34	99.88 ^a	98.82	98.45
4	99.33	99.82 ^b	98.76	98.25
6	99.19	99.88 ^a	98.78	98.04
SE ±	0.1492	0.0171	0.1236	0.1790
Interactions				
Concentration × Biochar	NS	NS	**	NS
Concentration × Shaking Time	NS	**	**	**
Biochar × Shaking Time	NS	NS	**	NS
Concentration × Biochar × Shaking Time	NS	NS	**	NS

Means followed by different letter(s) are significantly different at 5% level of probability

** = significant at 5%

Table 3 provide an overview of the adsorption of Pb by the interaction between concentration and shaking time. The concentration of Pb (mgkg^{-1}) shows significant difference ($p>0.05$) with regards to shaking time. At 2 hours shaking time, sorptions of Pb (99.87%, 99.90% and 99.88%) were statistically similar with regard to initial concentrations. However, at 4 hours, 50mgkg^{-1} concentration of Pb produced the least sorption (99.72%) which was statistically different from sorptions observed on 100mgkg^{-1} (99.86%) and 200mgkg^{-1} (99.90%). The best sorption (99.86%) was observed at 6hours on 100mgkg^{-1} concentration of Pb which was statistically similar to sorption (99.88%) on 200mgkg^{-1} but differs statistically from sorption (99.80%) observed 50mgkg^{-1} .

Table 3: Interaction between different concentration of Lead (Pb), biochar dose and shaking time on adsorption efficiency percentage.				
Treatments		Concentration of Heavy Metal (mgL^{-1})		
Shaking Time (hour)		50 (%)	100 (%)	200 (%)
2hrs		99.87 ^{ab}	99.90 ^{ab}	99.88 ^{ab}
4hrs		99.72 ^c	99.86 ^{ab}	99.90 ^{ab}
6hrs		99.80 ^{bc}	99.96 ^a	99.88 ^{ab}
SE±		0.0231		

Table 4 shows the influence of sorption of Zn by the interaction between concentration, shaking time and doses of biochar used. The concentration of Zn differs significantly ($p< 0.05$) with regard to shaking time and biochar dose.

At 0.2g biochar rate, the sorptions recorded with 2hours, 4hours and 6hours shaking times at 200mgkg^{-1} concentration of Zn (99.44%, 99.40% and 99.48%) were statistically the same and higher as compared to the concentration at 100mgkg^{-1} . The sorptions at 100mgkg^{-1} (99.03%, 99.05% and 99.03%) were statistically the same all through the shaking time. However, the sorptions at 50mgkg^{-1} of Zn were observed to be the least and differ from each other with regard to shaking time (98.07%, 97.88 % and 97.81 %) respectively.

At 0.4g biochar dose, the trend was similar to 0.2g biochar where the sorption with 200mgkg^{-1} of Zn were statistically the same all through the shaking time (99.42%, 99.41% and 99.44%) and were higher as compared to 100mgkg^{-1} of Zn. The concentration of Zn at 100mgkg^{-1} produce sorptions that were statistically the same all through the shaking time (99.03%, 98.90% and 98.92%) respectively. The lowest sorptions were produced at 50mgkg^{-1} of Zn with the least sorption (97.77%) recorded at 6hrs shaking time.

Similarly, 0.6g biochar dose followed the same trend as compared to 2g and 4g biochar dose, however, the least sorption was observed at 50mgkg^{-1} of concentration Zn (97.83%) at 4hrs shaking time.

Table 4: Interaction between different concentration of Zinc (Zn), biochar rate and shaking period adsorption efficiency.				
Treatments		Concentration of Heavy Metal (mgL^{-1})		
Biochar (g)	Shaking time (Hrs)	50 (%)	100 (%)	200 (%)
0.2	2hrs	98.07 ^{de}	99.03 ^{bc}	99.44 ^a
	4hrs	97.88 ^{efg}	99.05 ^{bc}	99.40 ^a
	6hrs	97.81 ^{gh}	99.03 ^{bc}	99.48 ^a
0.4	2hrs	97.99 ^{ef}	99.03 ^{bc}	99.42 ^a
	4hrs	97.93 ^{efg}	98.90 ^c	99.41 ^a
	6hrs	97.77 ^h	98.92 ^{bc}	99.44 ^a
0.6	2hrs	98.00 ^{ef}	99.06 ^b	99.30 ^a
	4hrs	97.83 ^{gh}	99.01 ^{bc}	99.39 ^a
	6hrs	98.17 ^d	98.95 ^{bc}	99.45 ^a
SE±	0.0266			

Table 5 provides an overview of the adsorption of Cd ion by the interaction between concentration and shaking time. The concentration, of Cd mgkg^{-1} shows significant difference ($p<0.05$) with regards to shaking time. 20mgkg^{-1} concentration of Cd produce the best sorption (99.00%, 99.01%

and 99.05%) which were at par with regard to shaking time, followed by 5mgkg^{-1} concentration of Cd (98.44%, 98.60% and 98.36%) which sorption were statistically the same with regards to shaking time of 2, 4 and 6hours. The least sorption was observed at 10mgkg^{-1} concentration of Cd (96.72%) at 6hrs shaking time.

Table 5: Interaction between different concentration of Cadmium (Cd) and shaking time on adsorption efficiency.			
Treatments	Concentration of Heavy Metal (mgL^{-1})		
	5 (%)	10 (%)	20 (%)
Shaking time (Hrs)			
2	98.44 ^{ab}	97.91 ^{bc}	99.00 ^a
4	98.60 ^{ab}	97.11 ^{cd}	99.01 ^a
6	98.36 ^{ab}	96.72 ^d	99.05 ^a
SE±	0.1722		

4. DISCUSSION

4.1 Effect of Initial Concentration on Adsorption of Heavy Metals

From the results obtained, adsorption increased with increase in initial concentration for Pb, Zn and Cd as their best sorption percentages were observed at 200mg kg^{-1} indicating a better sorption at higher concentration of metals used, which can be attributed to the non-saturation of sorptive sites. When metal concentrations are low, the adsorbent's binding sites far exceed the available metal ions, preventing saturation. However, as the metal ion concentration increases, so does the metal uptake, until the adsorbent's capacity is fully utilized and saturation is reached. (Zubair et al., 2008, Liu and Zhang 2009, Chen and Chen 2011, Eneji et al., 2016). Meanwhile, it was observed that Cu had its best sorption at lower concentrations. This may be due to the fact that at lower concentration the ratio of Cu ion to the dosage of biochar is low, a rise in concentration implies that additional Cu ion are present in the mixture and hence more ion are attached to the same dose of biochar which result to saturation of the biochar causing a decrease in adsorption percentage. Similar observations were made by (Al-Homaidan et al., 2014; Meitei and Prasad, 2014). They claimed that a state of equilibrium was reached at a specific concentration of metal ions, where the biosorbent's active binding sites became fully saturated, resulting in a balance between the adsorbed metal ions (adsorbate) and the biosorbent. The same trend was also observed by Liu in 2008 who proposed that adsorption process may be dependent on the availability of adsorption sites on the surface of adsorbent rather than adsorbate concentration in the bulk solution (Liu, 2008). Generally, based on the values of the percentage of metal adsorption, the selectivity sequence of metal sorption onto biochar was found to be $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$. Relatively higher sorption affinity of Pb^{2+} can be explained by its large ionic radius (0.118 nm) as compared to Cd^{2+} (0.097 nm) and Cu^{2+} (0.073 nm). Many studies concerning the adsorption of heavy metals (Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+}) onto soils and pure minerals have reported that Pb^{2+} has a higher sorption affinity than other heavy metals (Saha et al., 2002; Usman 2008; Gao et al., 1997). Usman (2008) proposed a higher Pb^{2+} sorption selectivity relative to other metals (Cu^{2+} , Zn^{2+} , Ni^{2+} and Cd^{2+}) by the following reasons: (i) higher ionic radius, and subsequently smaller hydrated radius, (ii) higher atomic weight, (iii) greater first hydrolysis constant and therefore increased hydrolyzing ability.

4.2 Effect of (Biochar) Dosage on Adsorption of Heavy Metals

The result reveals that increasing the biochar dose across all the metals tested did not cause any significant change in percentage removal of metal ion, therefore did not singly affect the sorption of heavy metals under consideration. This behavior may be because, at initial stage there were sufficient binding sites for complexation of heavy metals ions and subsequently overlapping adsorption sites of adsorbent (biochar) occurred. This observation agreed with researchers who reported that, there were sufficient binding sites for complexation of metal ion at initial stage while increasing dosage to 6g/l did not cause any significant change in adsorption of metal ions as a result of the establishment of equilibrium between the metal ions bound to biochar and those remaining unadsorbed in the mixture (Igberase and Osifo, 2015; and Ozer, 2004).

4.3 Effect of Shaking Time on the Adsorption of Heavy Metals

Shaking time had no significant effect on the adsorption of Cu, Zn and Cd on biochar, however, a specific trend was observed across all the metal under test as equilibrium adsorption were attained within 2hours, reflecting rapid initial adsorption due to well aligned site available for the

binding of metal ions on biochar, it became slower subsequently with increase in time of contact indicating the maximum adsorption level as a saturation point. Similar result was reported which established that equilibrium time of 120 minutes is sufficient for the removal of different metals ions from solution (Rafatullah et al., 2009).

4.4 Interaction Between Concentration and Contact Time on the Adsorption of Pb Ion

The results obtained from the research shows that there is a significant difference in the interaction between concentration and shaking time on the adsorption of Pb ion. Better adsorption rate was observed at higher concentration. It was also observed that the rate of sorption was very fast in the first 2 hours, thereafter a gradual decrease in sorption at 4 hours and subsequent increase at 6 hours. This may be attributed to the availability of large surface area of the biochar or adsorption of metal ions into the exterior surface of biochar neglecting intra-particle diffusion. Most researchers also reported that adsorption slowed and eventually reached equilibrium as Pb ions occupied binding sites, causing repulsive forces that hindered further ion binding over time (Yalcin, 2014; Igberase and Osifo, 2015; Shanmugapriya et al., 2013). Similar results were obtained and was reported that the time taken to approach the equilibrium for Cd(II) and Pb(II), is between 120 to 180 minutes depending on the initial concentration in the systems described (Chen and Chen, 2011).

4.5 Interaction Between Initial Concentration and Biochar Doses on the Adsorption of Zn

From the study, it was found that the adsorption is dependent on initial metal concentrations with percentage removal increasing with increasing initial concentration of Zn ion from 50-200 mgkg⁻¹. Although the highest percentage removal was recorded at 200 mgkg⁻¹ (99.42%), and at biochar dosage of 0.2g. Increasing the biochar dose above 0.2g did not cause any outstanding changes in the adsorption efficiency. The observed behavior occurred because at the 0.2g biochar dose, there were sufficient binding site for the complexation of Zn ion resulting in establishment of equilibrium. Similar trend was previously reported stating that constant concentration of Zn ion removal beyond 1.2g of biochar was due to overcrowding of biosorbent particles as a result of excessive biochar dosage leading to overlapping of adsorption sites (Benias et al., 2019). It is evident that adsorption rate is rather fast at initial stage and then slow down gradually.

4.6 Interaction Between (Biochar) Dosage and Shaking Time on the Adsorption of Zn

The result shows that there was a sharp and rapid increase in percentage adsorption of Zn ion at initial; biochar dosage of 0.2g (≥ 97.81%) and increasing the biochar dose above 0.2g did not cause any outstanding changes in the adsorption efficiency irrespective of the shaking time. A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Similar result was obtained and was reported that the time to approach the equilibrium for Zn (II) is 120 minutes depending on the type of the adsorbent in the systems described (Abdus-salam and Adekola, 2018). Rapid adsorption of metal ions during the initial stage was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on the adsorbent surface (Chigondo et al., 2013).

4.7 Interaction Between Initial Concentration and Shaking Time on the Adsorption of Zn Ion

The result reveals that the Zn ion removal was very high within the initial 2hrs of shaking (≥ 98%) while adsorption was increasing with increasing concentration. This could be attributed to adsorption of Zn ion onto the exterior surface of biochar and the availability of more vacant surface binding sites (Song et al., 2013). This was followed by gradual Zn ion uptake due to ions diffusing into the interior surface. 2 hours contact time gave a good adsorption efficient time irrespective of the fluctuations as a result of saturation and repulsion between the adsorbed species and the bulk phase.

4.8 Interaction Between Initial Concentration and Shaking Time on the Adsorption of Cd Ion.

The result shows that there was a huge increase in percentage adsorption at the initial concentration of 5 mgkg⁻¹ then a slight decrease at 10 mgkg⁻¹ followed by a gradual increase which lead to the attainment of equilibrium at 20 mgkg⁻¹ with 99.02% adsorption. The adsorption was very fast at the initial stage for Cd ion due to sufficient coverage of the aligned site with Cd ion. Desorption process observed at 10 mgkg⁻¹ may be due to repulsion

which sets in with increase in time as result of saturation (Igberase and Osifo 2015, Ozer and Ozer 2004). Similar trend was observed in the system described by Chen and Chen who reported that 2 hours was sufficient to attain more than 97% adsorption efficiency of Cd which is an indication that higher adsorption of Cd ion is achievable with higher concentration within a shorter time (Chen and Chen, 2011). Contact time of between the ranges of 2-4 hours was established as the optimum contact time for the adsorption of Cd by (Naiya et al., 2009). This is important because longer contact time between adsorbent and adsorbate in solution can consume energy and hence increase cost of treatment.

5. CONCLUSION

The objective of this research was to evaluate the potential of maize-cob derived biochar on heavy metal adsorption. From the study, it can be observed that biochar used was suitable as a potential adsorbent with high sorption efficiency in the adsorption of metal. Adsorption was majorly influenced by concentration of metal ions. Sorption of the metal ions was also affected by both physical and chemical properties of biochar such as high porous structure, surface area, cation exchange capacity and adsorptive capacity.

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