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RESEARCH ARTICLE

EVALUATION OF BIOCHAR ON ADSORPTION KINETIC OF SOIL SOLUTION CONTAMINATED WITH HEAVY METALS

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ABSTRACT

Environmental contamination by heavy metals has become a world-wide problem. This is due to the fact that heavy metals contrary to other pollutants are non-biodegradable. Heavy metals (Cu, Pb, Zn and Cd) adsorption potential of maize-cob derived biochar and its property for improving the quality of irrigation water, was evaluated in this study. Soil samples from vegetable gardens were randomly collected around Jaba, while water samples were obtained across the irrigation water source (Jakara river). Both soil and water samples were digested using a mixture of HF- HNO_3-HCl and Aqua rijia respectively in order to determine the heavy metal content by AAS. Equilibrium and kinetic experiments were carried out to ascertain the effects of parameters such as 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) 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 hours, 4 hours and 6 hours using AAS. The adsorption data related well with the Freundlich isotherm model having correlation coefficient of $R^2 > 0.96$ for Cu and Pb, and $R^2 > 0.76$ for Zn whereas the adsorption kinetics corresponds with the pseudo-second-order model as adjudged by the high R^2 and low SE values recorded. This study shows that biochar derived from maize-cob is a promising and inexpensive adsorbent that can be used for metal ion removal from aqueous solutions in soil and improvement of irrigation water quality.

KEYWORDS

Heavy Metals, Biochar and Adsorption Kinetic

1. INTRODUCTION

Heavy metals constitute a global issue posing environmental and public health concern due to their toxicities, bioaccumulation in the human body and food chain, carcinogenicities, and mutagenesis in various living organisms (Wang et al., 2013; Sarka et al., 2014; Chowdhury et al., 2015). Growing human activity has escalated domestic and industrial wastes generation with the consequence of adding hazardous concentrations of heavy metals into water bodies, soil and the environment at large. Some heavy metals especially the transition metals (Cu, Ni, and Zn) are essential for plant metabolism but when in excessive concentration (Cd, Cr, Cu, Hg, As, Ni, Pb, and Zn) could be regarded as toxic and environmentally damaging. In recent years, environmental contamination by heavy metals has become a world-wide problem. This is due to the fact that heavy metals contrary to other pollutants, are non-biodegradable. Similar to many developing countries, Nigeria has poor environmental management and enforcement policies for wastewater. And owing to the scarcity of fresh water, domestic sewage and industrial effluent are important wastewater sources used for the irrigation of vegetables and other crops (Khan et al., 2008; Olayiwola and Bernard, 2016; Bayero et al., 2018). The use of wastewater for irrigation can contribute significantly in the increase of heavy metal content in the soil and food chain (Ullah et al., 2012; Hussain et al., 2013).

Removal of toxic substances resulting from the accumulation of domestic and industrial wastes has become inevitable, and adsorption is one of the methods used. Adsorption process is found to be a more effective and practicable method over other techniques for removing metals pollution. Adsorption technique is one of the easiest, safest and more cost- effective methods for heavy metal removal from industrial effluents (Shah et al., 2009; Rahmani et al., 2009). The term "adsorption" is defined as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions (Babel and Kurniawan, 2003). Previous studies have reported various models describing the mechanism that exist between the adsorbate and the adsorbent. The Langmuir model and Freundlich model are commonly used to describe the sorption isotherms while on the other hand, in terms of kinetics; the pseudo first order and pseudo second order kinetic models are used to describe the sorption kinetics.

Biochar has gained an acceptance in this regard and is increasingly being evaluated. Biochar is a solid carbon-rich by-product of a process called pyrolysis, which consists the heating of biomass (typically agricultural wastes) in an oxygen limited environment. Biochar possesses a number of remarkable properties including a high internal surface area, negative charge, and resistance to degradation, which make it suitable for the remediation of contaminated soils (Mukherjee et al., 2011). Having established by previous studies the existence of metal pollution, it has become expedient to solve the problem therein. Various methods of remediating soils polluted by metals exist; they range from physical to chemical and biological methods. Methods such as ion exchange, chemical and microbiological precipitation, among others have been developed and employed to remove heavy metals from water, but their use is limited due to their capital, labor and energy intensive nature. Also, there is little or scanty information about the understanding of the chemical dynamics of

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the process. 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.

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

2.1.1 Soil Sampling

Soil samples were obtained at depths of 0–20 cm, where most rooting activities of vegetables occur. The samples were collected randomly from 2 farms of less than 0.1 ha in size. And in each farm, five soil samples were collected. The five samples from each of the farms was bulked together to form a composite sample from which three portions were separated. These were air-dried, gently crushed with mortar and pestle, and then sieved on a 2mm sieve mesh. The sampled Soil was from vegetable farms in Jaba, along the Jakara river of Fagge Local Government Area, 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 a 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 undergoing the process of pyrolysis, the biochar was allowed to cool overnight before grounding it to small granules and later sieved over a 2mm sieve in order to obtain a uniform particle size as that of the soil.

2.3 Laboratory analyses

2.3.1 Soil analyses

Soil samples obtained from the field were subjected to laboratory analyses according to established procedures, as follows. All analyses were replicated three times. pH values were determined from EL model 720 pH meters using the 1:2.5 soil-water ratio; particle size was analyzed using the hydrometer method outlined in Adepetu et al., 2000. Using an EC meter (Janway 4520 model), EC of the soil samples having a soil–water ratio of 1:2.5 (as was used in pH determination) was obtained. The soil bulk density was determined using core sample method as outlined by 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^{o}C for 24 hours. The organic carbon content of the soil was determined using the Walkley-Black wet oxidation method as outlined in Adepetu et al., 2000. Due to the slightly acidic nature of the soils under investigation, the available phosphorus in soil was extracted using Bray 1 method (Bray and Kurtz, 1945), and the quantity determined using the Blue method (Drummond and Maher, 1995). Neutral ammonium acetate extraction technique (Jaiswal, 2004) was used in extracting the bases. Sodium and potassium contents was determined by flame emission, using an EEL Flame Photometer while Calcium and Magnesium contents was determined using Atomic Absorption Spectrophotometer (Agilent 200 Series, 240 FS).

The exchangeable acidity was determined by the Peech method; while total nitrogen was determined using the micro-Kjheldal Method outlined by Jaiswal (2004). Digestion tubes were soaked in 1M HCl for 24 hours before digestion and 1g of each soil fraction was weighed and placed in the presoaked digestion tubes. A mixture of HF-HNO_3–HCl in ratio of 2:6:1 was prepared and 9ml 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 50ml with distilled water. The total amount of Cu, Cd, Pb and Zn present in the solution was determined using AAS.

2.3.2 Determination of total heavy metals in Biochar

According to the procedure outlined by Lim and Jackson in 1986, the total content of Cu, Cd, Zn, and Pb in the biochar was determined by digestion of the biochar with a mixture of HCl-HNO_3 (Lim and Jackson, 1986). After digestion, the suspension was filtered over Whatman No. 42 filter paper into a 100ml volumetric flask and the total concentration of Cu, Cd, Zn, and Pb in the biochar was obtained 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.1g of soil: 0.2g of biochar, 1g of soil: 0.4g of biochar and 1g of soil: 0.6g of biochar).

The soil sample and biochar was transferred into the incubation vessels and 25ml each of the varying concentrations of heavy metal (50mgkg^{-1}, 100mgkg^{-1} and 200mgkg^{-1} for Cu, Pb and Zn, and 5mgkg^{-1}, 10mgkg^{-1}, 20mgkg^{-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% was reached, the samples were shaken on mechanical shaker for a period of 2, 4 and 6 hours. After each shaking period, twenty 20ml of the suspension was taken, filtered into a bottle and the amount of Cd, Cu, Pb and Zn left in the suspension was obtained using the AAS. The amount sorbed by the soil was calculated as:

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

2.5 Data analysis

The data was subjected to analysis of variance (ANOVA) using Genstat (Genstat, 17th edition)

The adsorption efficiency of each biochar was determined by

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

Where C_e = concentration at equilibrium

C_t = concentration at time t

The batch adsorption data was fitted to adsorption isotherms to obtain the best model. The adsorption isotherms used was: Freundlich adsorption isotherm and Langmuir adsorption isotherm. The kinetic data was fitted to the Pseudo-first order model, Pseudo-second order model and intra particle diffusion model to evaluate adsorption process.

The coefficient of determination (R^2) was used to determine the goodness of fit and the standard errors for estimating the kinetic parameters. The standard error was calculated as follows:

$$SE = \sum \left[\frac{(P_a - P_b)^2}{n-2} \right]^{0.5} \quad (3)$$

Where;

Pa is the experimentally determined P sorbed,

Pb is the calculated amount of P sorption estimated by the kinetic models,

and n is the number of measurements.

3. RESULTS

3.1 Physical and chemical properties of soil and biochar

The initial condition of the soil is shown in Table 1. The soil has a mean of 20.45% soil moisture content, and a medium to high soil bulk density of 1.62g/cm^3. 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 was 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 as shown in the Table 1 below:

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

Soil properties	**Soil**	**Biochar**
SMC (%)	20.45	1.01
Bulk density (g/cm³)	1.62	-
pH in H_2O	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 Textural class	7.653 Loamy sand	-
TN (g/kg)	0.7	10.1
Av.P (mg/kg)	9.623	33.06
K (cmol/kg) Cu (mgkg^{-1}) Pb (mgkg^{-1}) Zn (mgkg^{-1}) Cd (mgkg^{-1})	0.499 0.06 0.0532 0.7472 0.0557	3.81 0.017 0.017 0.360 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 isotherm models

Sorption isotherm models were investigated for 0.2g, 0.4g and 0.6g doses of biochar using the initial concentration of 50 mgkg^{-1} and shaken for 2hrs. Two isotherm models, namely Freundlich and Langmuir were employed. Table 2 shows the results of Freundlich and Langmuir sorption isotherm models parameter values for the removal of Cu ion by biochar. The regression equation and R² values for the models are presented in Figures (1) and (2) respectively. The Freundlich model shows a good fit for the sorption of Cu with R² value between 0.97-1 for all the different doses of biochar considered. The highest R² value was observed at 0.2g and lowest was observed on 0.6g biochar dose. However, the value of n is greater than 1 ranging from 2.8-2.96, while the K_f value was observed to be between 2.3 to 2.5. The Langmuir model had also good fit with its R² value between (0.93-0.98). There were also relatively low qe and K_l value for the model. The higher R² value in the Freundlich model therefore made the Cu sorption by biochar better explained by the model. Table 2 shows results of Freudlich and Langmuir sorption isotherm models parameter values for the removal of Pb ion by biochar. The regression equation and R² values for the models are presented in figures (3) and (4) respectively.

The Freundlich model was observed to have a better fit for the adsorption of Pb expressing a very high R² value of 0.96 on both 0.2 g and 0.6g biochar doses respectively. R² value of 0.74 was observed at 0.4g dose of biochar. The n values were generally very low (0.124, 0.153 and 0.148) for 0.2g, 0.4g and 0.6g respectively. K_f value ranged from 1.78 to 2.23. Unlike Freundlich model, Langmuir showed a relatively poorer fit compared to Freundlich. Similar to the Freundlich model however, 0.4g of biochar also had the lowest fit (0.563) for the model. Table 2 illustrates the various Freudlich and Langmuir sorption isotherm models parameter values for the removal of Zn ion by biochar. The regression equation and R² values for both models are presented in Figures (5) and (6), respectively. The best sorption fit as demonstrated by R² value was observed at biochar dose of 0.2g (0.778) using the Freundlich model. Much poorer fit was recorded by the Langmuir model, except the fairly higher value at biochar dose of 0.2g (0.605). Other parametric values for both models especially the model constants (K_f and K_l) were similarly higher for the Freundlich model (K_f = 2.635) than the Langmuir (K_l= 0.012). Table 2 shows results of Freudlich and Langmuir sorption isotherm models parameter values for the removal of Cd ion by biochar. The regression equation and R² values for the models are depicted in Figures (7) and (8), respectively. Langmuir model was observed to have a better fit for the adsorption of Cd expressing R² value of 0.829 and 0.975 on 0.2g and 0.4g biochar doses respectively. R² value of 0.706 was recorded at 0.6g biochar dose. A good R_l values were also observed on all the doses under consideration.

Unlike Langmuir model, Freundlich model showed a relatively poorer fit in the sorption of Cadmium ion. Similar to Langmuir model however, 0.4g biochar dose was observed to have the highest fit (0.931)

Table 2: Freundlich and Langmuir isotherm constants and coefficient of determination (R2) for sorption of Cu, Pb, Zn and Cd ion on different doses of biochar

Cu Model	Parameter	Biochar Doses		
		0.2g	0.4g	0.6g
Freundlich	Kf	2.842	2.541	2.351
	N	2.967	2.941	2.833
	R2	1	0.975	0.971
Langmuir	qe	0.00004	0.00002	0.00005
	Kl	0.0009	0.0022	0.0034
	Rl	1	0.83	0.86
	R2	0.981	0.936	0.935
Pb				
Freundlich	Kf	2.229	2.028	1.781
	N	0.124	0.153	0.148
	R2	0.963	0.744	0.965
Langmuir	qe	0.019	0.029	0.051
	Kl	0.015	0.021	0.037
	Rl	0.571	0.323	0.119
	R2	0.874	0.563	0.879
Zn				
Freundlich	Kf	2.635	2.292	2.144
	N	0.139	0.188	0.273
	R2	0.778	0.563	0.517
Langmuir	qe	0.014	0.020	0.020
	Kl	0.012	0.014	0.020
	Rl	0.625	0.417	0.294
	R2	0.605	0.357	0.301
Cd				
Freundlich	Kf	1.432	1.136	1.000
	N	0.832	0.695	1.438
	R2	0.628	0.931	0.429
Langmuir	qe	0.042	0.090	0.080
	Kl	0.004	0.016	0.025
	Rl	0.980	0.862	0.667
	R2	0.829	0.975	0.706

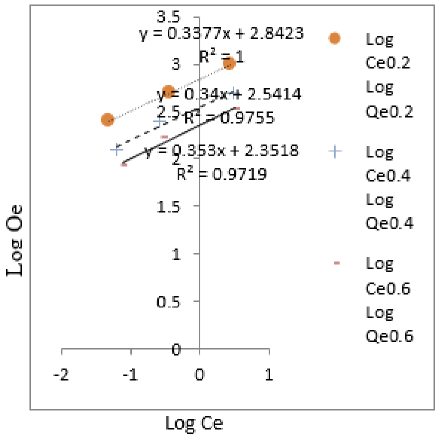

Figure 1: Freundlich Model: Cu

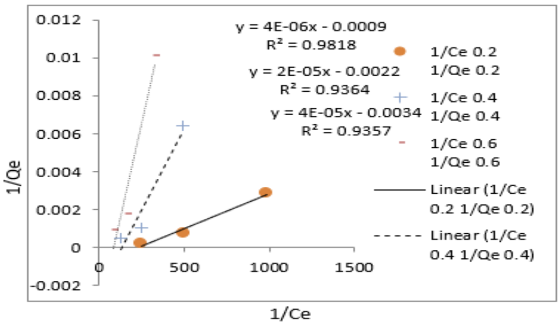

Figure 2: Langmuir Model: Cu

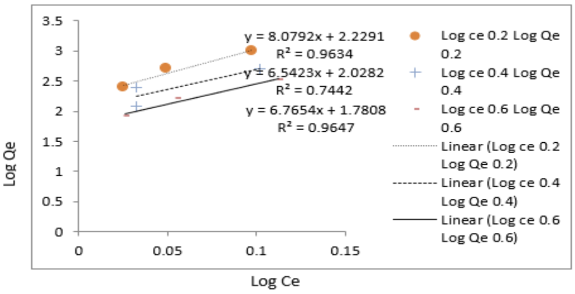

Figure 3: Freundlich Model: Pb

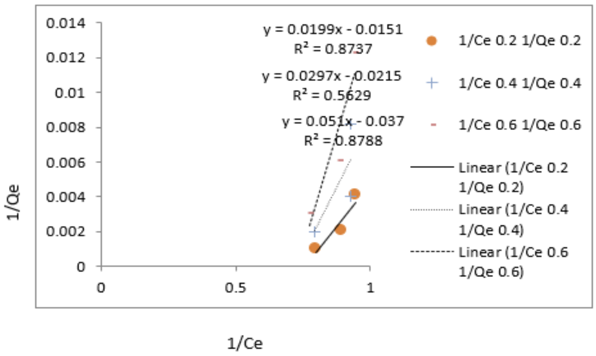

Figure 4: Langmuir Model: Pb

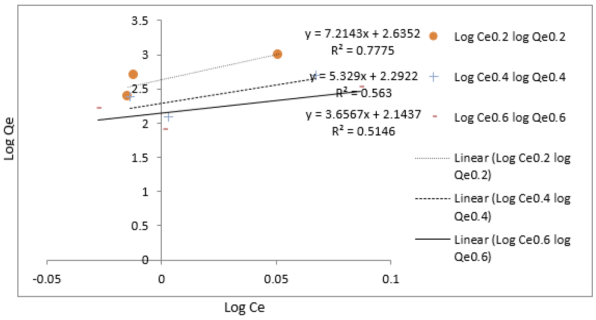

Figure 5: Freundlich Model: Zn

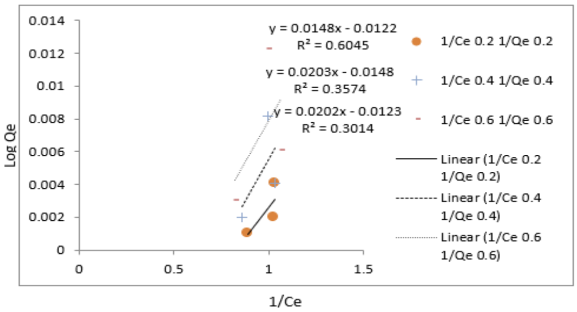

Figure 6: Langmuir Model: Zn

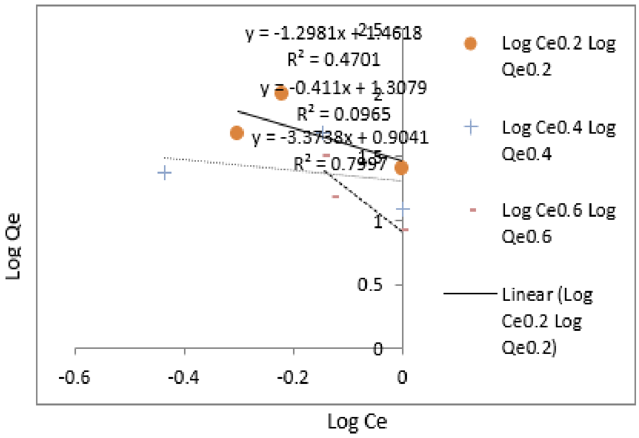

Figure 7: Freundlich Model: Cd

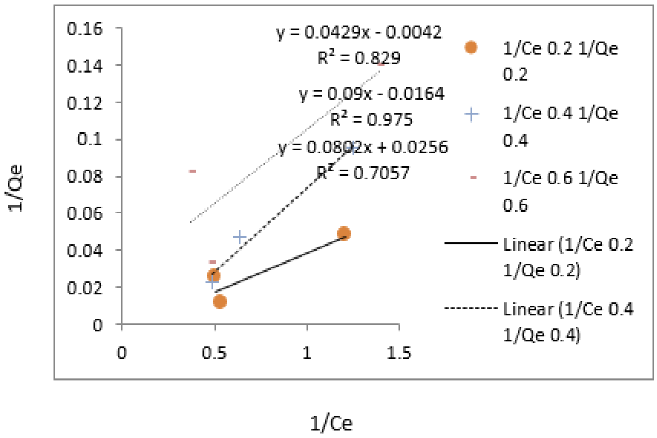

Figure 8: Langmuir Model: Cd

3.4 Adsorption kinetics

The adsorption data was subjected into pseudo second order model and obtained parameters were presented on Table 3. High values of pseudo second order rate constant were noted for all the metals involved. Cu recorded its highest R^2 value (0.999) under 0.6g dosage of biochar in 50 mgL^{-1} concentrations and lowest (0.988) on 0.4g biochar dose in 100 mgL^{-1} concentrations.

The R^2 values for Pb and Zn among the two metal concentrations (50 mgL^{-1} and 100 mgL^{-1}) and biochar doses (0.2g, 0.4g and 0.6g) were > 0.97. Both metals recorded their highest R^2 value on 0.2g biochar dose in 50mgl^{-1} concentration as 0.999 and 1.000 respectively. Cadmium had its best R^2 value (0.999) and lowest R^2 value (0.816) at 6g biochar dose in 5mgL^{-1} and 10mgL^{-1}, respectively.

The pseudo second constant (K_2) was below 1 in all the metals concentration under consideration. However, Cd ion had few exceptions where K_2 value was >1 particularly on 0.6g biochar dose in 5mgL^{-1} concentration and 0.4g biochar dose in 10mgL^{-1}concentration.

For the adsorption per minute per gram (Qe), the highest Qe value for Cu and Pb of less than 1 (i.e 0.913 and 0.988) was observed on 0.2g of biochar dose in 50mgL^{-1} and 0.2g of biochar at 100mgL^{-1}, respectively, whereas Zn and Cd ion had their best Qe value to be >1 on 0.2g biochar in 200mgL^{-1} and 0.2g biochar in 5mgL^{-1}, respectively.

From Table 4 and 5, R^2 value of pseudo second order model and intra particle diffusion model was far lower than the pseudo second order model as majority of the R^2 values were less than 0.999 making them considerably less fit for the data.

Similarly, Table 6 shows that the standard error values of Pseudo first order model were very high (>1 in Cu, Pb and Zn, and > 0.2 in Cd) as compared to the standard error values observed in Pseudo second order and intra- particle diffusion models (< 0.3).

Table 3: The pseudo-first order model constants for the adsorption of the different metals and at different level of biochar

Copper					**Lead**					**Zinc**					**Cadmium**				
Conc. (Mgl^{-1})	**Biochar (g)**	**Qe (mgg^{-1})**	**K_1 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_1 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_1 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_1 (gmg^{-1}g^{-1})**	**R^2**
50	0.2	0	3.89	0.128	50	0	0	3.891	0.999	50	0.2	0	3.893	0.936	5	0.2	0.006	1.421	0.56
50	0.4	0	3.891	0.5	50	0.4	3.00E-05	3.889	0.006	50	0.4	0	3.892	0.932	5	0.4	0.003	1.433	0.425
50	0.6	-8x10^{5}	3.89	0.795	50	0.6	0	3.8	0.029	50	0.6	0	3.89	0.261	5	0.6	-0.017	1.501	0.108
100	0.2	0	4.591	0.141	100	0.2	0	4.593	0.477	100	0.2	-5x10^{-6}	4.595	0.007	10	0.2	0.052	2.175	0.97
100	0.4	0	4.592	0.507	100	0.4	0	4.593	0.095	100	0.4	0	4.595	0.656	10	0.4	0.063	2.249	0.98
100	0.6	-7x10^{-5}	4.591	0.307	100	0.6	0	4.593	0.651	100	0.6	0	4.595	0.583	10	0.6	0.005	1.997	0.995

Table 4: The pseudo second order model constants for the adsorption of the different metals and at different level of biochar

Copper					**Lead**					**Zinc**					**Cadmium**				
Conc. (Mgl^{-1})	**Biochar (g)**	**Qe (mgg^{-1})**	**K_2 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_2 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_2 (gmg^{-1}g^{-1})**	**R^2**	**Conc. (Mgl^{-1})**	**Biochar (g)**	**Qe (mgg^{-1})**	**K_2 (gmg^{-1}g^{-1})**	R^2
50	0.2	0.913	0.013	0.996	50	0.2	0.812	0.287	0.999	50	0.2	0.936	0.361	1	5	0.2	1.48	0.408	0.993
50	0.4	0.892	0.144	0.997	50	0.4	0.936	0.097	0.994	50	0.4	0.932	0.342	0.996	5	0.4	1.418	0.207	0.994
50	0.6	0.907	0.049	0.999	50	0.6	0.91	0.055	0.987	50	0.6	0.261	0.491	0.977	5	0.6	0.797	1.618	0.816
100	0.2	0.65	0.153	0.988	100	0.2	0.988	0.286	0.993	100	0.2	0.007	0.038	0.999	10	0.2	0.177	0.644	0.997
100	0.4	0.724	0.13	0.997	100	0.4	0.987	0.257	0.985	100	0.4	0.656	0.275	0.997	10	0.4	0.113	1.024	0.963
100	0.6	0.72	0.075	0.998	100	0.6	0.981	0.278	0.995	100	0.6	0.583	0.195	0.997	10	0.6	0.337	0.07	0.999

Table 5: Intra-particle diffusion model constants for the adsorption of the different metals and at different level of biochar

Copper					**Lead**			**Zinc**			**Cadmium**				
Conc. (mgl^{-1})	**Biochar (g)**	**H (mgg^{-1})**	**K_d (gmg^{-1}g^{-1})**	**R^2**	**H (mgg^{-1})**	**K_d (gmg^{-1}g^{-1})**	**R^2**	**H (mgg^{-1})**	**K_d (gmg^{-1}g^{-1})**	**R^2**	**Conc. (mgl^{-1})**	**Biochar (g)**	**H (mgg^{-1})**	**K_d (gmg^{-1}g^{-1})**	**R^2**
50	0.2	0.034	1.019	0.182	0.104	0.910	0.996	0.124	0.796	0.968	5	0.2	-0.111	0.965	0.632
50	0.4	0.033	1.006	0.424	0.000	1.099	5.00E-06	0.099	0.856	0.89	5	0.4	-0.067	0.875	0.497
50	0.6	0.013	1.057	0.731	0.034	1.047	0.061	-0.074	1.146	0.198	5	0.6	0.26	0.3	0.636
100	0.2	0.041	1.364	0.093	0.066	1.234	0.402	0.000	0.966	7.00E-05	10	0.2	1.472	0.053	0.984
100	0.4	0.045	1.224	0.431	0.032	1.157	0.056	0.116	0.823	0.726	10	0.4	1.848	1.001	0.99
100	0.6	0.023	1.303	0.239	0.072	1.253	0.577	0.042	0.932	0.508	10	0.6	0.154	2.488	0.979

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Table 6: The Standard Error values of the different metals of different kinetic models

	Concentration(mgl^{-1})	Biochar (g)	Pseudo- First Order	Pseudo-Second Order	Intra-Particle Diffusion
Cu	50	0.2	1.100	0.133	0.016
	50	0.4	1.101	0.099	0.010
	50	0.6	1.100	0.123	0.029
	100	0.2	1.363	0.099	0.143
	100	0.4	1.363	0.105	0.089
	100	0.6	1.362	0.119	0.119
Pb	50	0.2	1.101	0.068	0.026
	50	0.4	1.100	0.111	0.045
	50	0.6	1.066	0.122	0.026
	100	0.2	1.362	0.071	0.096
	100	0.4	1.360	0.076	0.063
	100	0.6	1.362	0.072	0.099
Zn	50	0.2	1.010	0.055	0.069
	50	0.4	1.100	0.058	0.046
	50	0.6	1.099	0.034	0.063
	100	0.2	1.361	0.029	0.090
	100	0.4	1.360	0.073	0.063
	100	0.6	1.362	0.090	0.022
Cd	50	0.2	0.223	0.021	0.049
	50	0.4	0.224	0.048	0.013
	50	0.6	0.244	0.105	0.210
	100	0.2	0.519	0.009	0.283
	100	0.4	0.531	0.002	0.059
	100	0.6	0.479	0.095	0.065

4. DISCUSSION

4.1 Adsorption Isotherm Models

The role of adsorption isotherm models in predicting the nature of adsorbate-adsorbent interaction, is of primary importance. In order to deduce the mechanism of metal ion adsorption from aqueous solution by the adsorbent, the experimental data obtained were fitted into Langmuir and Freundlich isotherm models, of which Freundlich adsorption models were found to have good fit for Cu, Pb and Zn while Langmuir expressed appropriate fit for Cd.

The value of n>1 in the sorption of Cu irrespective of the biochar dose used indicated the favorable nature of adsorption under Freundlich model. The value of n>1 suggests heterogeneity on the biomass surface and the metal ions were favorably and intensively adsorbed (Rahman and Sathasivan, 2015).

Freundlich adsorption model also was found to be favorable for the sorption of Pb and Zn as the values of n were found to be < 1 and the value of 1/n was > 1 in all the biochar doses under consideration. A study reported that an adsorption process with n-value < 1 is a chemical process Kumar et al., 2010). The value of 1/n>1 indicates a cooperative adsorption process (Aisha et al., 2017; Dhir and Kumar, 2010). A study described cooperative adsorption process as a means of idealization of a nonideal adsorption, where apparent multilayer adsorption has been shown to be descriptive of both physosorption and chemisorptions (Liu, 2015).

However, Langmuir adsorption model fits considerably better on the adsorption of cadmium than Freundlich. The value obtained for the Langmuir constant (K_l) indicates the irreversibility of the isotherm (Ho et al., 2002). The separation factor (R_l) was in the range of 0-1 decreasing with increasing adsorbent level which indicate favorable uptake of Cd ion.

4.2 Adsorption Kinetics

Adsorption kinetics provides requisite information for determining the adsorption rate controlling mechanism. The most frequently used integrated linearized kinetic model: Pseudo first order and pseudo second order, and intra particle diffusion were used to analyze the experimental data of all the metal ions (Cu, Pb, Zn and Cd).

From the results obtained, it was observed that the value of the pseudo-first order regression coefficient (R^2) was lowest among the studied kinetic models. Coefficient of determination (R^2) values as low as 0.1, 0.006, 0.007 and 0.1 were recorded on Cu, Pb, Zn and Cd respectively. Pseudo first order rate constant (K_1) was observed to increase with increase in concentration of metal ion, but the rate of adsorption per minute (q_e) recorded was low, indicating that adsorption did not take place immediately rather equilibrium was reached after few hours. Furthermore, the Standard Error (SE) of pseudo first order was high (> 1 in Cu, Pb, Zn and > 0.2 in Cd) as compared with pseudo second order model. Therefore, the kinetic data of Cu, Pb, Zn and Cd cannot be well described by pseudo first order model.

However, the pseudo second order rate constant (K_2) was found in the range of 0.013 to 0.491 in all the metals under consideration which supports that metal ion uptake from the aqueous solution onto the adsorbent was more rapid and favorable, (Rahman and Sathassivam, 2015).

The rate of adsorption per minute (q_e) was observed to decrease with increase in concentration of Cu, Zn and Cd, and agrees with the findings of (Aisha et al., 2017 and Liu, 2008). Liu, proposed that in a pseudo second order reaction; adsorption rate may depend on the availability of sorption site, rather than the total concentration of metal ions in the solution (Liu, 2008).

Unlike, pseudo first order, the value of regression coefficient (R^2) in pseudo second order was high. Coefficient of determination (R^2) values greater than 0.97 was recorded in Cu, Pb and Zn while ($R^2 > 0.8$) was observed on Cd, irrespective of the dosage of biochar or concentration of metals. With this, it may be said that adsorption process of metal ions was chemosorption controlled. Furthermore, the Standard Error (SE) was observed to be low (< 0.14) in all the metal under consideration. It can therefore be concluded that pseudo second order model best explains the kinetic adsorption of metal ions.

Intra-particle diffusion model was also observed to be unsuitable in describing the data as judged by the graphs which were not linear. This is an indication that adsorption of metal ions into an adsorbent involves more than one step. The first step involves mass transfer of adsorbate to the external surface of an adsorbent while intra-particle transport of the adsorbate into the pore of the adsorbent occurs in the second step. In this study, the intra-particle diffusion model cannot be regarded as a rate-limiting step because the R^2 values of intra-particle diffusion model is lower than that for Pseudo second order model, as can be seen in table 6, (Adeyinka 2019).

5. CONCLUSION

Adsorption of all the metal ions with the exception of Cd was adequately depicted by the Freundlich adsorption isotherm base on higher R^2 value. Langmuir isotherm had a good fit for adsorption of Cu and Cd metal ions but fail to adequately describe adsorption of Zn and Pb by the biochar. The mechanism of adsorption kinetics is suitably explained by the PSEUDO-second order model base on observed R^2 value as well, while Pseudo-first order model and Intra particle diffusion model had a poor fit for the studied data.

Adsorption was majorly influenced by concentration of the metal ions. The Sorption of metal ions was also affected by both chemical and physical properties of the biochar, such as; high porous structure, surface area, cation exchange capacity and adsorptive capacity.

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