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Goat Horn Biochar as a Low-Cost Adsorbent for the Removal of Cadmium and Zinc ions in Aqueous Solution

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Abstract: *Given the high toxicity of most heavy metal ions in aquatic environments and the need for remediation using environmentally friendly methods, this study was conducted to produce biochar from goat horn. The removal efficiency of the synthesised biochar in the removal of cadmium (Cd^{2+}) and zinc ($(Zn^{2})^{+}$) ions from aqueous solutions was also investigated. The proximate analysis of the goat horn biochar was carried out, the moisture content, ash content and bulk density were 10.62%, 6.5% and 0.79g/cm^3 respectively. FTIR characterization shows the function group of O-H, C=H, C-O, C=C and P-O. SEM analysis shows a distinct porosity and irregular surfaces with roughness. The batch adsorption experiment was also implemented to obtain information on the influence of pH, metal concentration and contact time on the removal efficiency of the biochar. The results of the study indicated that the optimal conditions for the removal of the metal ions was a pH of 7, 20mg/L. The adsorption equilibrium was obtained after 60 and 90 minutes of contact for Cd^{2+} and Zn^{2+}respectively.The adsorption data fitted the Langmuir isotherm with a correlation coefficient (R^2> 0.94) and suggested a uniform distribution of bonding energy between the Cd^{2+} and Zn^{2+} on biochar. The maximum adsorption capacity was 38.84 mg/g for Cd^{2+} and 33.692 mg/g for Zn^{2+}. The kinetic study enlisted the pseudo-second-order as the best-fitted model. The adsorption was proposed to be facilitated by the chemisorption mechanism.*

Keywords*:* Toxic metal, adsorption, goat horn biochar, isotherm, kinetic

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1.0 Introduction

Water is one of the most essential elements needed in our life, agriculture and industries (Eddy and Garg, 2021). However, the greatest challenge facing water demand is the quality and not the availability of water(Eddy and Ekop, 2007;Talat, 2020). Potable water is good for drinking and the potability is based on its standard composition. The presence of unwanted substances in water has several contamination consequences (López-Pacheco *et al*., 2019). One of the most common and most dangerous water contaminants is heavy metal ions (Bolisetty *et al*., 2019). They constitute water pollution when their concentrations are above certain permissible limits (Zamora-Ledezma *et al*., 2021).

Cadmium and zinc are bivalent heavy metal ions. Although the toxicity of zinc manifests at excessively high concentrations (5 mg/L), compared to that of cadmium (0.005 mg/L).Cadmium and zinc are known as association elements due to their similar mobility in the earth's crust.. Cadmium (Cd^{2+}) is one of the most toxic heavy metals. It is harmful even at low exposure levels and has acute and chronic effects on health and the environment. Acute symptoms include vomiting, diarrhoea, shortness of breath and destruction of mucous membranes. Chronic toxicity such as liver harm, bone degeneration, blood damage, and renal dysfunction are observed (Hayat *et al.*, 2019). Zinc (Zn^{2+}) is an essential heavy metal in the human body and it is required in trace amounts for the functional integrity of many organ systems, as well as for growth, development, and tissue repair (Sarasamma *et al.*, 2018). Exposure to excessive concentration of zinc can reveal acute symptoms such as diarrhoea, liver failure, bloody urine, icterus, kidney failure, stomach cramps, abdominal cramps, epigastric pain, nausea, and vomiting. It chronic symptoms include pancreatic harm, anaemia, and lower levels of high-density lipoprotein cholesterol (Dardouri *et al*., 2018).

Consequently, public health protocols required for the sustenance of water pollution must embrace all measures taken from the point of generation to the point of discharge. Major routes necessary for the introduction of heavy metal ions to the aquatic environment are heavy metal industrial effluences (Ali *et al*., 2020; Obasi and Akudinobi 2020; Yeleliere *et al*., 2018). Therefore, the treatment of such effluences before discharge forms the fundamental step towards the control of their discharge. Some of the established methods that have been tested and applied include; chemical precipitation, ion exchange, adsorption, reverse osmosis, electro-dialysis, filtration, coagulation, flocculation and floatation (Raouf *et al*., 2019). However, deep research and practical preferences have been directed towards adsorption because the method is flexible, cost-effective and can be designed to synchronize with standard practices, without much harm to the environment (Ameri *et al*., 2020). The applications of some plant and animal wastes as adsorbents has been encouraged in recent times because it seem to play a dual role of waste management (i.e. resource recovery) and then remediation course (adsorption removal of contaminants)(Li *et al*., 2019). Consequently, several documented resources from the abattoir sector are in use. For example, cow horn, chicken feathers, cow hoof and animal bone resources have been used for the treatment of water.

The present study is aimed at investigating the adsorption capacity if biochar produced from goat horns.

2.0 Materials and Methods

2.1 Sample collection and preparation

Goat horns were collected from a dumpsite at the Dogarawa goat market along Kano-Zaria, road, Kaduna state. They were thoroughly washedand sun-dried for a month. The dried horns were ground to a powdered form using mortar and pestle.The crushed goat horns (200g) were placed in large crucibles and the set-up was kept in a muffle furnace at a temperature of 400°C for 3hrs in the absence of air, after which they were removed and kept in a desiccator to allow to cool(Lateef *et al*., 2019). The biochar was ground to a size of 355 μm (44 BSS mesh size), 0.5 M HCl was used to wash and purify the carbon, then rinsed severally with distilled water and oven-dried before activation. The biochar was chemically activated using 1M H_3PO_4. It was impregnated with H_3PO_4 at the ratio of 1:2 with the aid of a stirrer and was placed in the muffle furnace operated at a temperature of 500°C for 1 hour (Yahya *et al*., 2015). The activated biochar was re-insed several times with distilled water to a neutral pH of 7 and finally dried in an oven at 110°C for 2 hours.

Stock solutions of Cd^{2+} and Zn^{2+} were respectively prepared by dissolving 0.2744g and 0.4550g of $Cd(NO_3)_2.4H_2O$ and $Zn(NO_3)_2.6H_2O$ in 1 dm^3 deionised water respectively. From the stock solutions, serially diluted solutions (20 - 60 ppm) of the metal ions solution were prepared respectively. These solutions were used for the development of calibration curves for the respective metal ions.

2.2 Proximate analysis

The moisture content (M.C), ash content (A.C) and bulk density(B.D)were determined as described by (Aller*et al*., 2017).

$$MC(\%) = \frac{(M_{BD}-M_{AD})}{M_{BD}} \times 100 \quad (1)$$

where; M_{BD}= mass of sample (g) before drying, M_{AD}= mass of sample (g) after drying

$$\text{A.C}(\%) = \frac{\text{Ash Weight (g)}}{\text{Oven Dry Wt.(g) of sample}} \times 100 \quad (2)$$

where; Ash weight weight after taken from the furnace, Oven dry weight weight of the sample before taken into the furnace.

$$B.D(\frac{g}{cm^3}) = \frac{M_{CS}-M_C}{V} \quad (3)$$

where; M_{CS} = mass of cylinder and sample, M_C = mass of empty cylinder, V = volume of cylinder

2.3 Characterization of the goat horn biochar

The Fourier Transform infrared spectrophotometer (Cary 630 FTIR, Agilent Technology, USA) with a wavenumber range of 400 to 4000 cm^{-1} was used to obtain information about the characteristic functional groups on the produced goat horn biochar. The surface morphology of the biochar was visualized using a scanning electron microscope (SEM Phenom ProX, England) coupled with an energy-dispersive X-ray spectrometer operating at 15 kV.

2.4 Batch adsorption studies

The adsorption studies were carried out at room temperature adopting the methods reported elsewhere. Investigated variables included concentration (20 – 60 mg/dm^3), pH (5.0, 6.0 and 7.0) and contact time (5, 15 and 30 minutes). All experiments were conducted using an adsorbent dosage of 2.0 g/dm^3 while the temperature was 303 K. Design-Expert software version 12, a full factorial design was used for the batch experiment.

The batch adsorption experiment was carried out at room temperature on a mechanical shaker (Gallenkamp, England) at 300 rpm, 0.1 g of goat horn biochar was introduced into 50 mL of Cd and Zn ions solutions in the different conical flask. For the series of measurements, the initial concentration of $Cd^{2+}$and Zn^{2+}solution ranges 20–60 mg/L. After shaking to each desired contact time (5-30 mins), samples were filtered and the concentration of the residual ions in the solution was determined using an Atomic absorption spectrophotometer (Varian AAS240, Agilent Technology, USA).The equilibrium concentration of metal ions adsorbed (Qe) and percentage removal (%R) from the solution using equations 4 and 5 respectively(Onanuga *et al*., 2021).

$$\text{Qe} = \frac{(C_o-C_e)V}{m} \quad (4)$$

$$\%\text{R} = \frac{(C_o-C_e)}{C_e} * 100 \quad (5)$$

where; Qe (mg/g) = amount of metal ions adsorbed,Co (mg/L) = initial metal concentration in solution, Ce (mg/L) = final metal concentration in the solution,V (L) = volume of the metal solution used in litre and m (g) = mass of the biosorbent.

2.5 Theoretical models

2.5.1 Adsorption isotherm

Adsorption isotherms are models that express the relationship between the concentration of the adsorbate and the degree of surface covered or the equilibrium amount of adsorbate adsorbed at constant temperature (Isiuku *et al*., 2021). The Langmuir isotherm assumes that monolayer adsorption exists at all surface sites that are homogeneity, with the ability of no interaction of adsorbed molecules with the neighbouring adsorption sites. The non-linear Langmuir model can be written as follows (Putro *et al*., 2017).

$$\text{Qe} = Qmax\frac{K_LCe}{1+K_LCe} \quad (6)$$

where; Qe(mg/g) is the adsorption capacity at equilibrium, Qmax(mg/g) = Theoretical maximum adsorption capacity of the adsorbent, Ce (mg/L) = Equilibrium concentration of the system, K_L (l/mg) = Langmuir affinity constant.

The favourability of the adsorption process or isotherm is dependent on the dimensionless constant R_L, which can be evaluated using equation 7

$$R_L = \frac{1}{1+K_L Co} \quad (7)$$

where; Co is the initial metal concentration.

The non-linear model of the Freundich isotherm relates Q_e with C_e according to equation 8

$$Qe = KfCe^{1/n} \quad (8)$$

where; Kf (mg/g) = Freundlich constant related with adsorption capacity, n = heterogeneity coefficient (dimensionless)

2.5.2 Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetics canprovide information about the dynamics of the adsorption of $Cd^{2+}$and Zn^{2+} on goat horn biochar.

The Lagergren pseudo-first-order kinetic model was givenas adopted byGupta and Singh, (2018).

$$\frac{dQt}{dt} = K_1 ad(Qe - Qt) \quad (9)$$

The integrating and simplification of equation 9yieldsequation10.

$$Qt = Qe(1 - e^{-k_1 t}) \quad (10)$$

where;K_1 (min^{-1}) = rate constant of the pseudo-first-order adsorption, Qt (mg/g) = amount of adsorption at time t (min), Qe (mg/g) = amount of adsorption at equilibrium, t (min) = time

The equation for the Pseudo-second-order equation is given as follows;

$$\frac{dQt}{dt} = K_2 ad(Qe - Qt)^2 (11)$$

The integrating and simplification of equation 11yields equation 12 (Moussout *et al*., 2018).

$$Qt = \frac{Qe^2 k_2 t}{1+Qek_2 t} (12)$$

where; k_2 = rate constant of second-order adsorption (g mg^{-1} min^{-1}).

3.0 Results and Discussion

3.1 Proximate analysis of the biochar

The moisture content, ash content and bulk density of biochar were 10.62 ± 0.12 %, 6.5± 0.20% and 0.57 ± 0.00 g/cm^3 respectively. The measured moisture content is comparable to those reported by others (Kolodynska *et al*., 2012). Ash content indicates the amount of inorganic matter content on the biochar, lower ash content can favour the average activity of the biochar towards metal removal (Bentley, 2020). Denver (1991) suggested that bulk density greater than 0.25 g/cm^3 indicates a suitable adsorbent for toxic metal removal. Therefore, based on this limit, the produced biochar is expected to be a good adsorbent for the removal of heavy metal ions.

3.2Characterization of the biochar

The FTIR spectrum of the goat horn biochar is shown in Fig. 1. The spectrum reveals a peak at 3201cm^{-1} representing O-H stretching vibration of alcohol, phenol, or carboxylic acid, At 2959 cm^{-1}a peak corresponding to C-H stretching vibration in methyl group of an alkane group, The observed peak at 2113 $cm^{-1}$is due to the C≡C stretching vibration peak 1640 cm^{-1} is typical for C=O and C=C stretching vibrations, C-O group was found at 1438 cm^{-1} Peaks between 1066 $cm^{-1}$and 931 cm^{-1} are consequences of P-O bonding of the phosphoric acid through PO_2 and PO_3 (Liu & Fan, 2018).

The FTIR spectrum of biochar after adsorption of Cd^{2+} and Zn^{2+} indicates a shrunk and broadened of O-H, C-H, C-O and P-O peaks as shown in Figs. 2 and 3. Adsorption of Cd^{2+} and Zn^{2+} on biochar causes a shift in O-H peak from 3291 to 3198 & 3179 cm^{-1}respectively, while C-H peak shifted from 2959 to 2929 cm^{-1}, C-O peak shifted from 1144 to 1170 cm^{-1} and P-O peaks from 931 & 1055 cm^{-1} to 898 and 1077 $cm^{-1}$for Cd^{2+} and Zn^{2+} respectively. This confirms that there is interaction between the adsorbent and the adsorbate after the adsorption process (Eddy *et al*., 2022)

The SEM image of the goat horn biochar is in Fig.3. It is evident from the micrograph that the biochar possesses some irregular and rough surfaces with several cracks having distinct porosity with the deduction closely aligned with the work of Miandad *et al.* (2018).The SEM micrographs of the biochar after the adsorption of Cd^{2+} and Zn^{2+} (Figs. 5 & 6) differ from the one presented in Fig. 4 because of the impregnation of the surface of the adsorbent by the metal ions, which led to a more arranged surfaces and provide evidence that adsorption occurred.

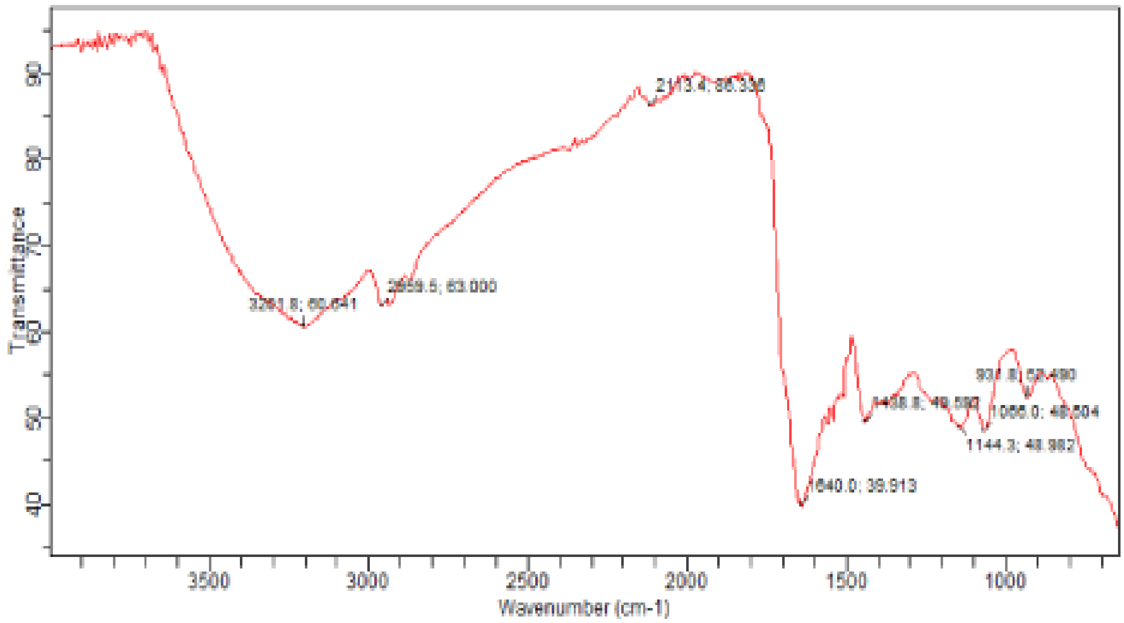

Fig.1: FTIR of goat horn biochar

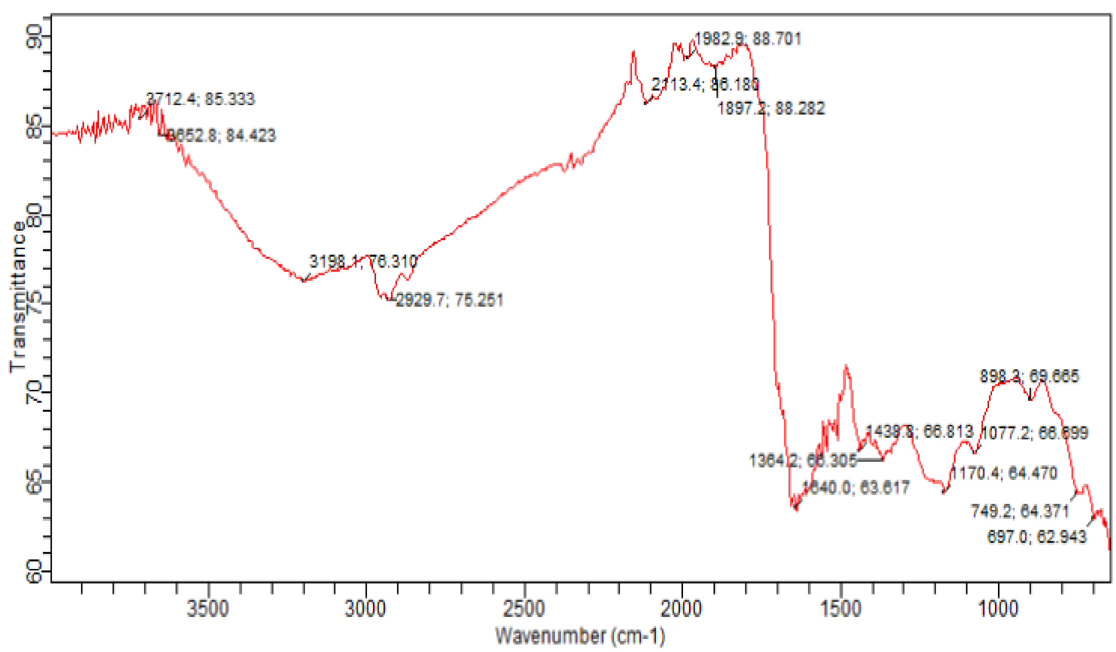

Fig. 2: FTIR of biochar after adsorption of Cd^{2+}.

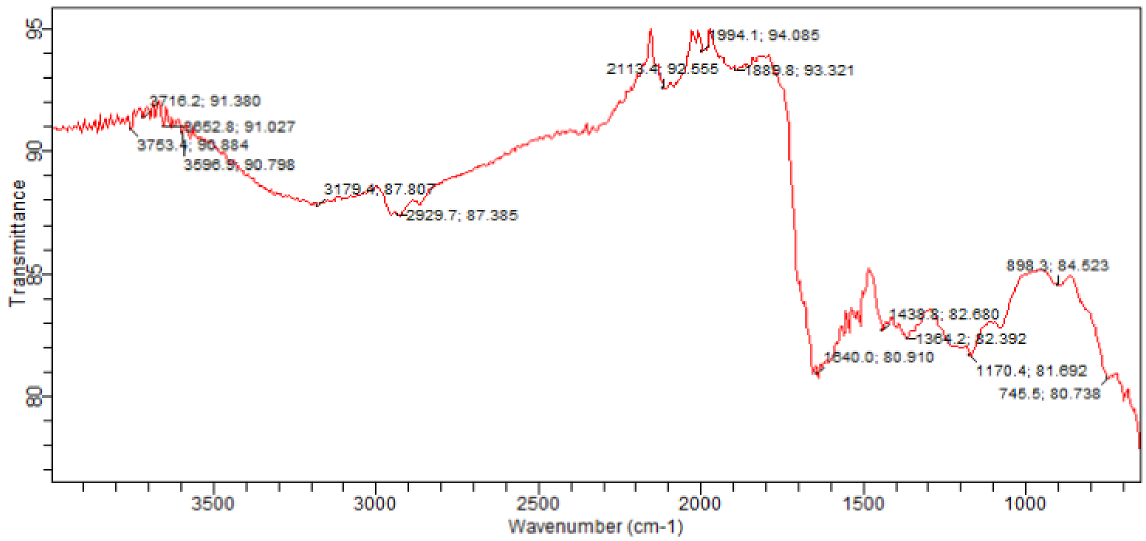

Fig. 3: FTIR of biochar after adsorption of Zn^{2+}

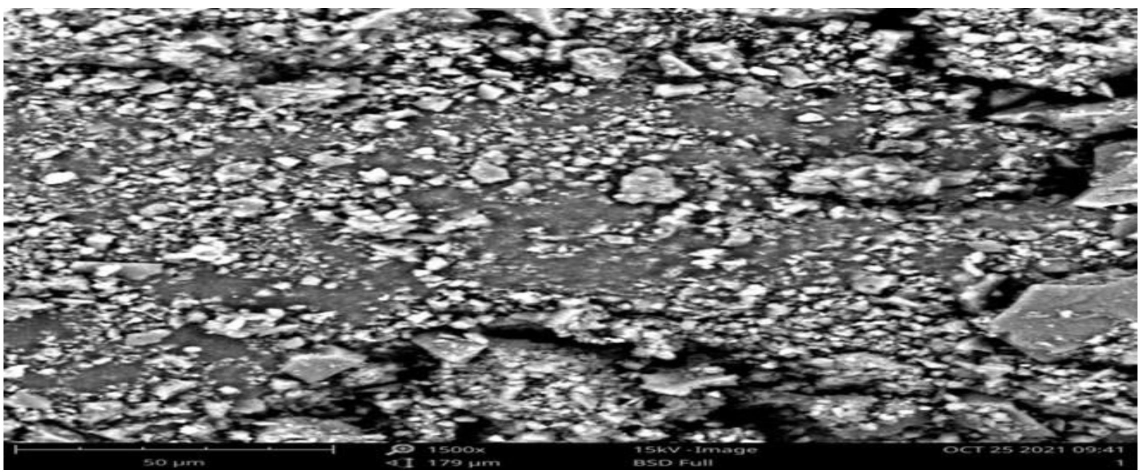

Fig. 4: Scanning electron micrograph of goat horn

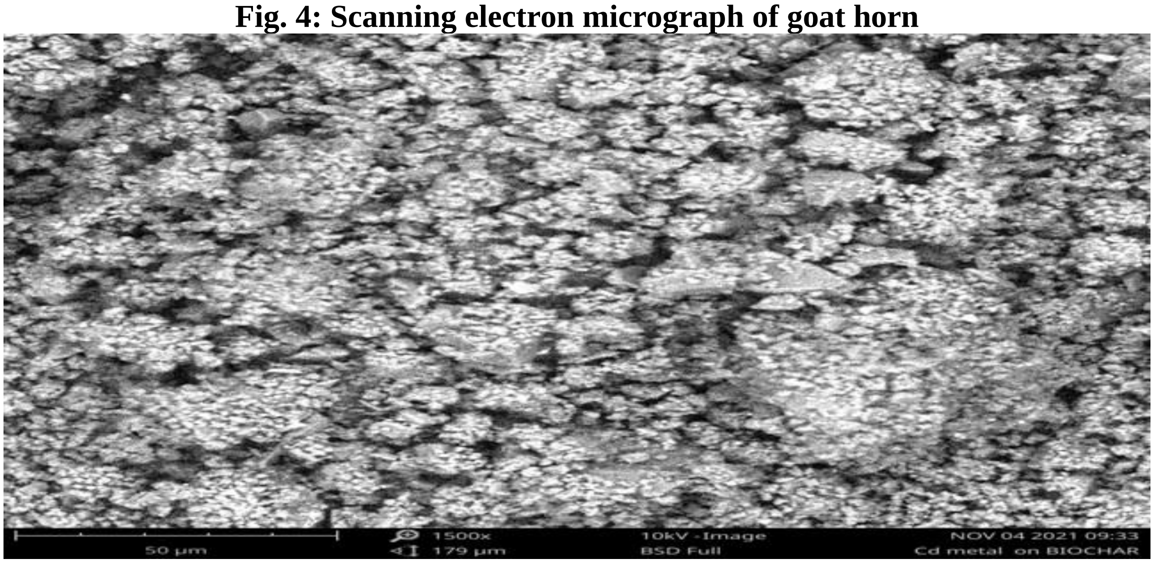

Fig. 5: Scanning electron micrograph of biochar after adsorption of Cd^{2+}

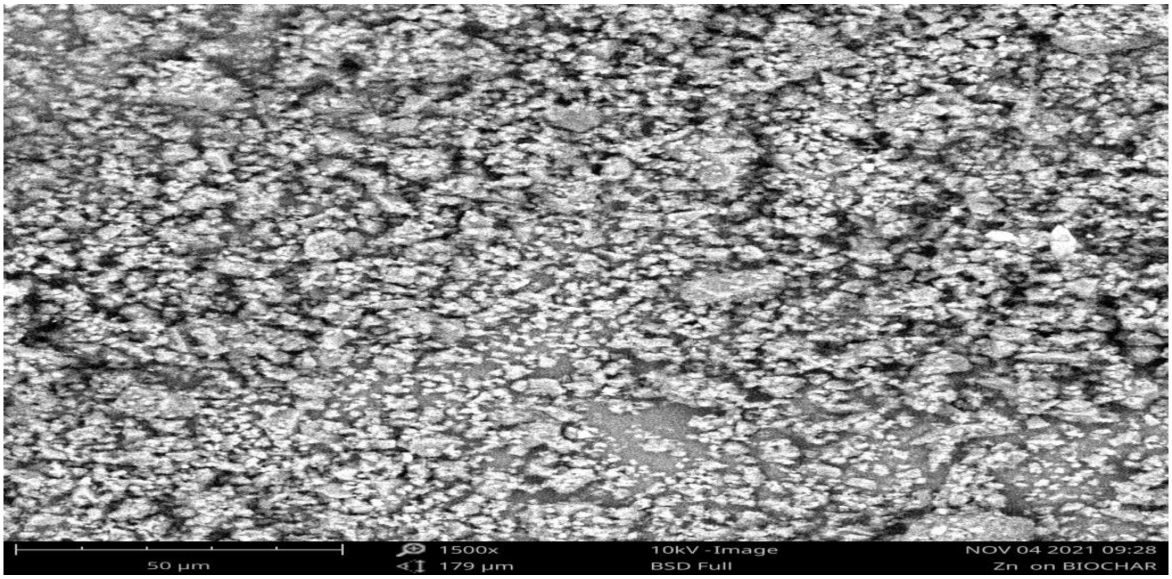

Fig. 6: Scanning electron micrograph of biochar after adsorption of Zn^{2+}*3.1.2Batch adsorption study*

Fig.7 shows the effect of pH on the percentage (%) removal of Cd^{2+} and Zn^{2+} in water at 20 mg/L and at 30 mins. An increase in % removal was observed as pH increased from 5 to 7 for both Cd^{2+} and Zn^{2+}. The %removal of Cd^{2+} and Zn^{2+} by the biochar at pH 5 was 55 and 49%, while at pH 6 was 70 and 82% respectively. This may be due to the competition between hydrogen ions and metal ions for the available binding sites. The adsorption of the studied metal ions becomes more feasible when the affinity for the adsorption favours the metal ions more than the H^{+}. Such affinity is controlled by pH (Odoemelam *et al*., 2018). From Fig. 7, the adsorption of the metal ions increases with an increase in pH because the release of hydrogen ions does not favour adsorption. In this work, alkaline pH was not considered but it maybe meaningful to state that beyond the neutral pH, the extent of adsorption of these metal ions may decrease (Shen *et al*., 2015).

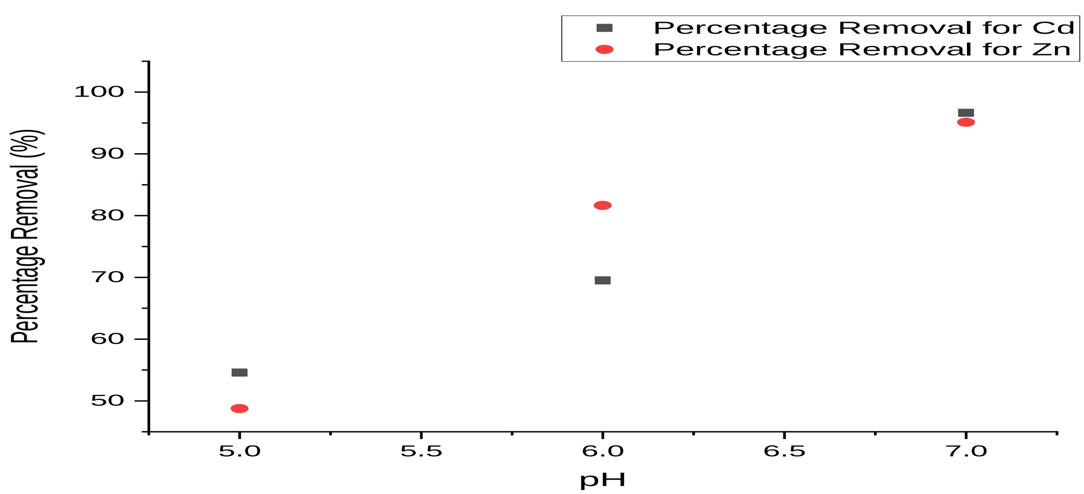

Fig. 7: Effect of pH on percentage adsorption of Cd^{2+} and Zn^{2+}on biochar

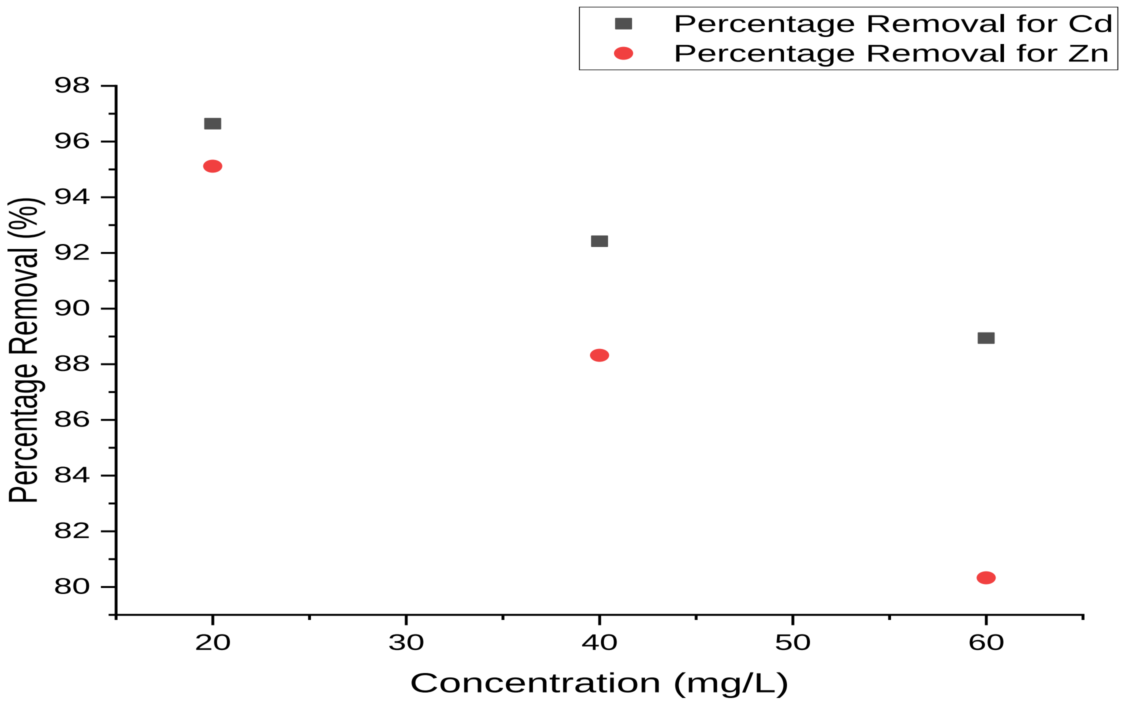

Fig. 8:Variation of percentage removal with the initial concentration of Cd^{2+} and Zn^{2}

Figure 8, shows the effect of concentration on percentage removal at pH 7 after 30 minutes period of contact. It isobserved that as concentration increases from 20 to 40 mg/L, the % removal decreases from 97 to 92% and 95 to 88% respectively. Further increase in concentration from 40 to 60 mg/L resulted in a corresponding decrease from 92 to 88%and from 88 to 80% for Cd^{2+} and Zn^{2+}respectively. Dawood *et al*. (2017) and several researchers have explained the observed trend for the variation of the amount of heavy metal ions adsorbed with the initial concentrations of the metal ions. Thus there exists a fixed number of active adsorption sites that must be occupied by the metal ions. Once these sites have been occupied, further increase in concentration will not lead to an increase in the amount of metal ions adsorbed but can rather encourage desorption.

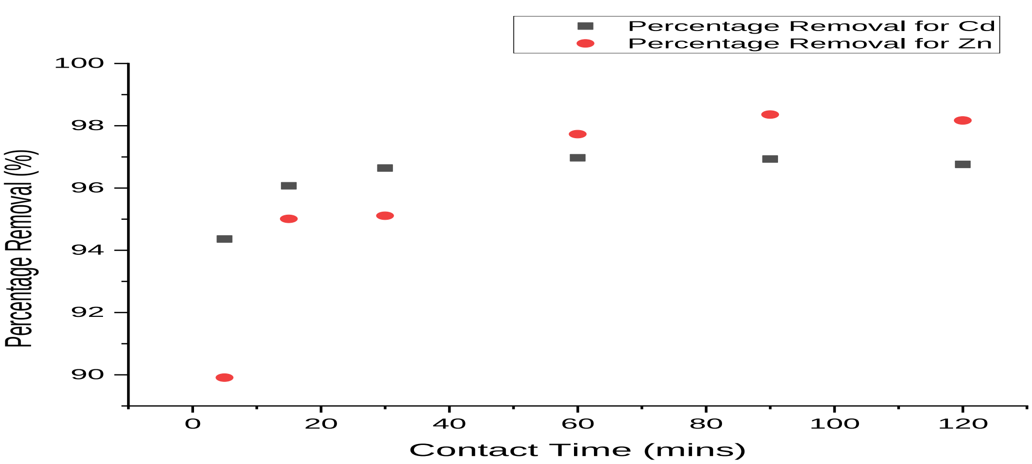

Fig. 9:Variation of percentage heavy metal ion removed with the period of contact

The variation of the amount of metal ions adsorbed with time is shown in Fig. 9. The study was conducted using an initial metal ion concentration of 20 mg/L and between a time interval of 5 to 120 minutes while the pH was 7. The plots revealed that an increment in contact time from 5 to 60mins increased the % removal of $Cd^{2+}$from 94.36 to 96.97% while the increment in contact time from 5 to 90 mins increased the % removal of Zn^{2+} from 89.91 to 98.36%. This is due to the gradual penetration and occupation of the active adsorption sites as the period of contact increases. Consequently, after the saturation of the available active adsorption sites, further increase in time led to desorption, which is, a decrease in the amount of heavy metal ion adsorbed Several studies have reported similar findings and ascribed such trends to reasons explained in this work (Eddy, 2009; Kumar *et al*., 2021).

2.3 Adsorption isotherm

The Langmuir isotherm for the adsorption of Cd^{2+} and Zn^{2+} are shown in Figs. 10 and 11. The Langmuir constant (K_L) was 0.4670 and 0.3993 while the estimated maximum adsorption capacity (Qmax) were 38.844 and 33.6918 mg/g for Cd^{2+} and Zn^{2+} respectively. Therefore, the biochar adsorbed Cd^{2+} more than Zn^{2+}.This can be attributed to differences in ionic characteristics of $Cd^{2+}$and Zn^{2+} including electro-negativity (1.69 and1.65) and ionic radii (0.097 and0.083) (McKay and Porter (1997). The R^2-values for the fitted Langmuir isotherms were 0.9432 and 0.9913 for Cd^{2+} and Zn^{2+}as shown in Table 1.The Langmuir dimensionless constants (R_L) were 0.0967 and 0.1001 for Cd^{2+} and Zn^{2+} respectively. The $R_L$values indicate the adsorption process was favourablesince they aregreater than 0 but less than 1(Dawood *et al*., 2017).

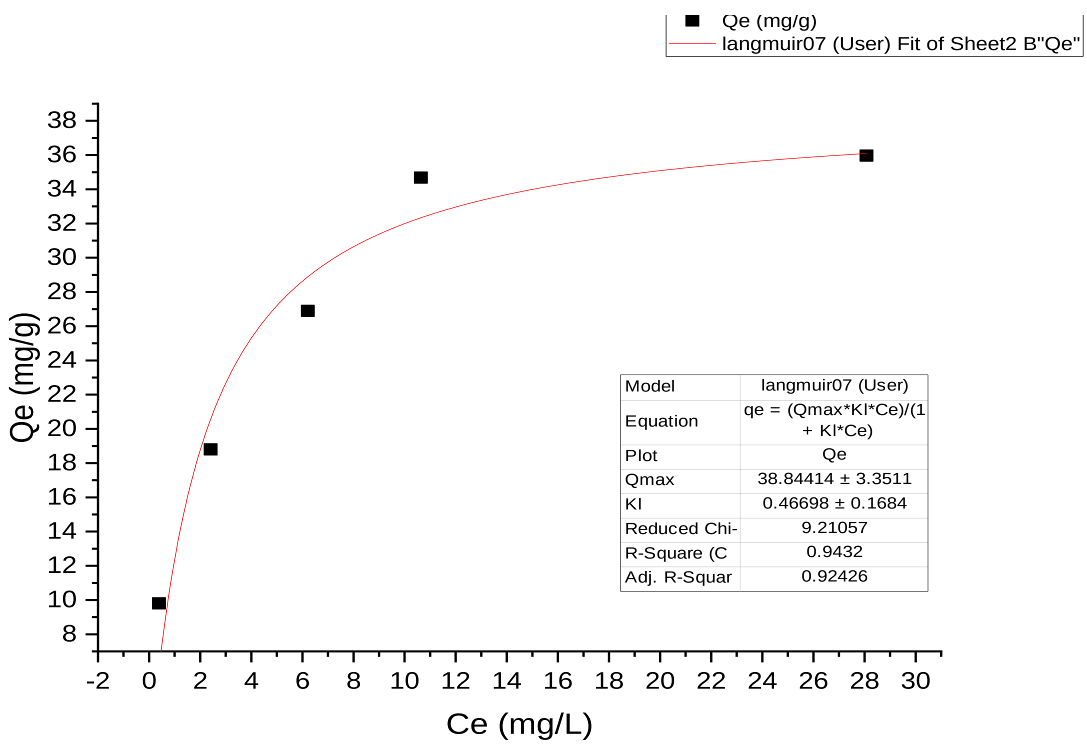

Fig.10: Langmuir isotherm for the adsorption of cadmium ions bythe biochar

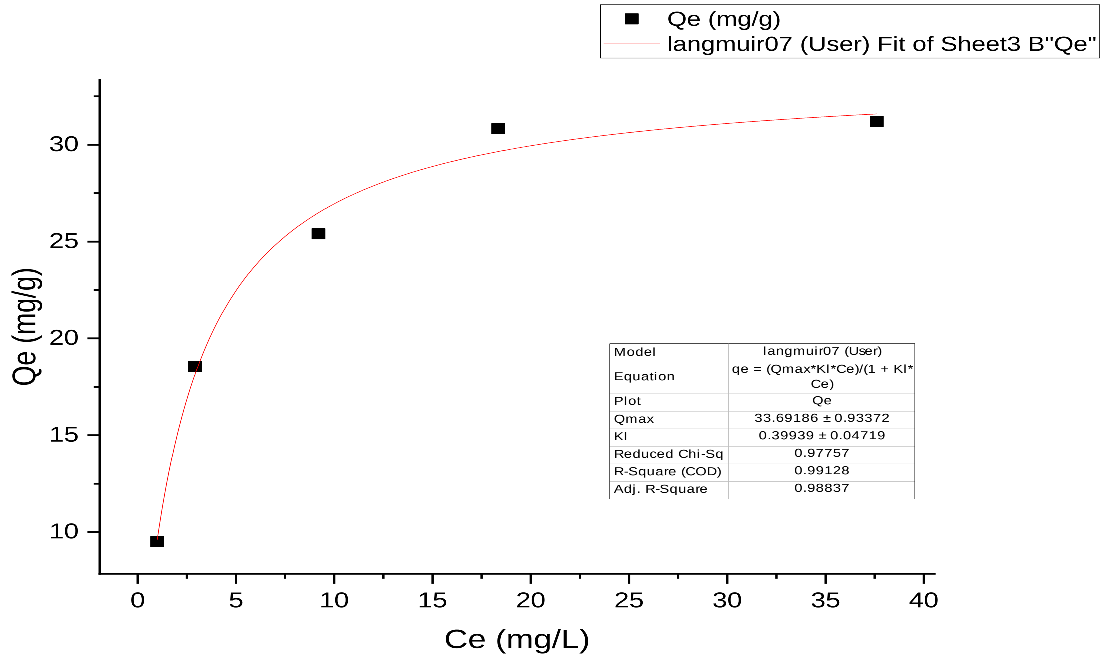

Fig.11: Langmuir isotherm for the adsorption of zinc ions by the biochar

The Freundlich isotherm for the adsorption of Cd^{2+} and Zn^{2+} by the biocharare shown in Figs. 12 & 13 respectively. The Freundlich constant (K_F) for Cd^{2+} and Zn^{2+} are 15.7193 and 13.0969 respectively, which are consistent with values reported for good adsorption when compared with literature values. The *n*-values are 3.6727and 3.8053, indicating a favourable and feasible adsorption process as the *n*-value ranges from1-10 (Kumar *et al*., 2021). The R^2 values were 0.9189 and 0.9019 for Cd and Zn ions respectively (Table 2).

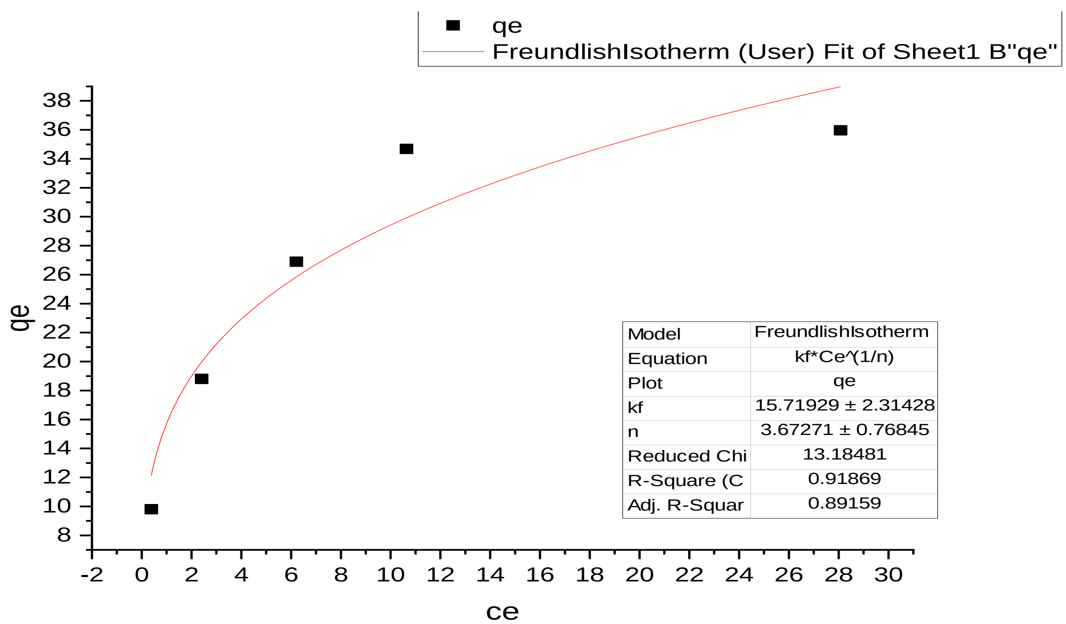

Fig.12: Freundlich isotherm forthe adsorption of cadmium ions by the biochar

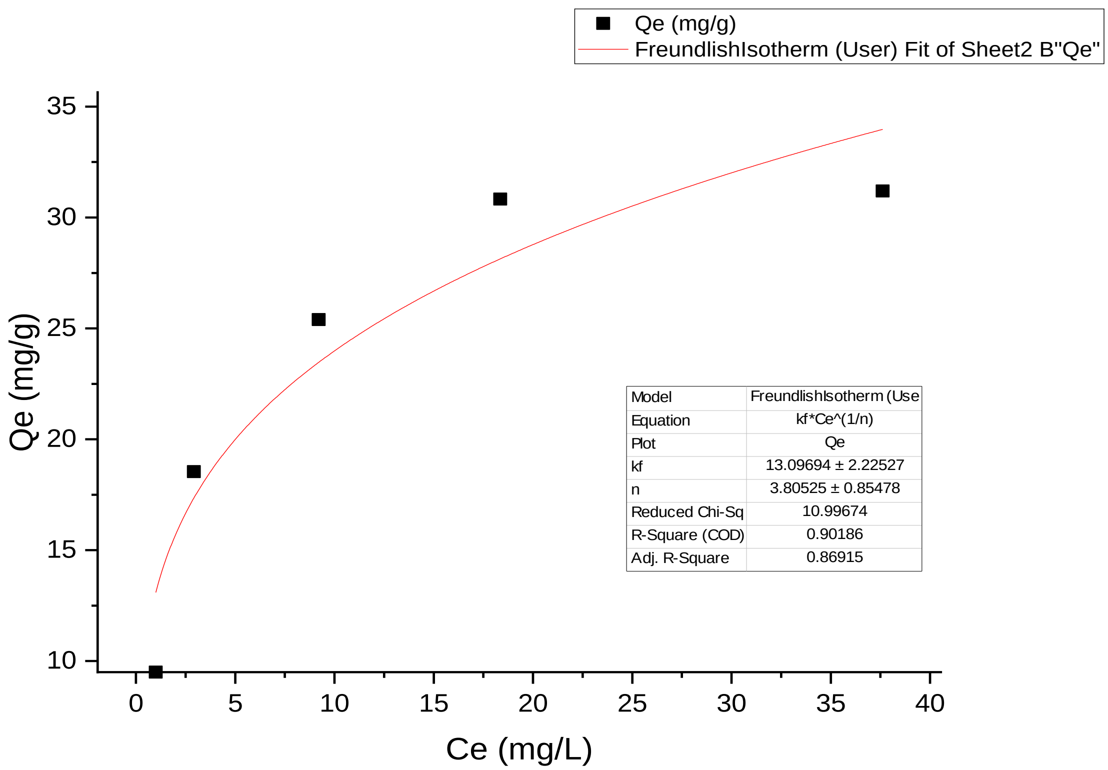

Fig.13: Freundlich isotherm forthe adsorption of zinc ions by the biochar

Table3: Langmuir and Freundlich parameters for the adsorption of Cd^{2+} and Zn^{2+} by the biochar

	Langmuir				**Freundlich**		
	Qmax(mg/L)	**K_L** (L/mg)	**R_L**	**R^2**	K_F(L/mg)	***n***	**R^2**
Cd^{2+}	38.844	0.4670	0.0987	0.9432	15.7193	3.6727	0,9189
Zn^{2+}	33.6918	0.3993	0.1001	0.9913	13.0969	3.8053	0.9019

3.3 Adsorption kinetic

Pseudo-first-order and second-order models were relatively significant in the description of the adsorption kinetics of Cd^{2+} and Zn^{2+} on biochar as shown in Table 4. The calculated adsorption capacity (q_{cal}) for $Cd^{2+}$and Zn^{2+} were 9.697 and 9.7050 mg/g respectively.The R^2values for the pseudo-first-order kinetic were 0.8948 and 0.7890 for $Cd^{2+}$and Zn^{2+}respectively. The corresponding,$q_e$values were9.6675 and 9.6869 while the K_1 values were 0.7463 and 0.5259 respectively (Figs. 14 & 15).The pseudo-second-order kineticstudy gave R^2 values of 0.9878 and 0.9403, q_e values of 9.7050 and 9.8142 mg/g and K_2 is 0.7211 and 0.2156 for Cd^{2+} and Zn^{2+} respectively as shown (Figs. 16 & 17). Based on the evaluated values of the degree of linearity and the values of Q_e, the pseudo-second-order kinetic fit the kinetic of the adsorption of Cd^{2+} and Zn^{2+} best. Similar reports have been published by others includingZand and Abyaneh (2020) for the adsorption of Cd^{2+} by biochar, Khan *et al*.(2020) by magnetic biochar and Mustapha *et al*., (2019) for the adsorption of Pb, Cu, Zn and Cd by plant materials.

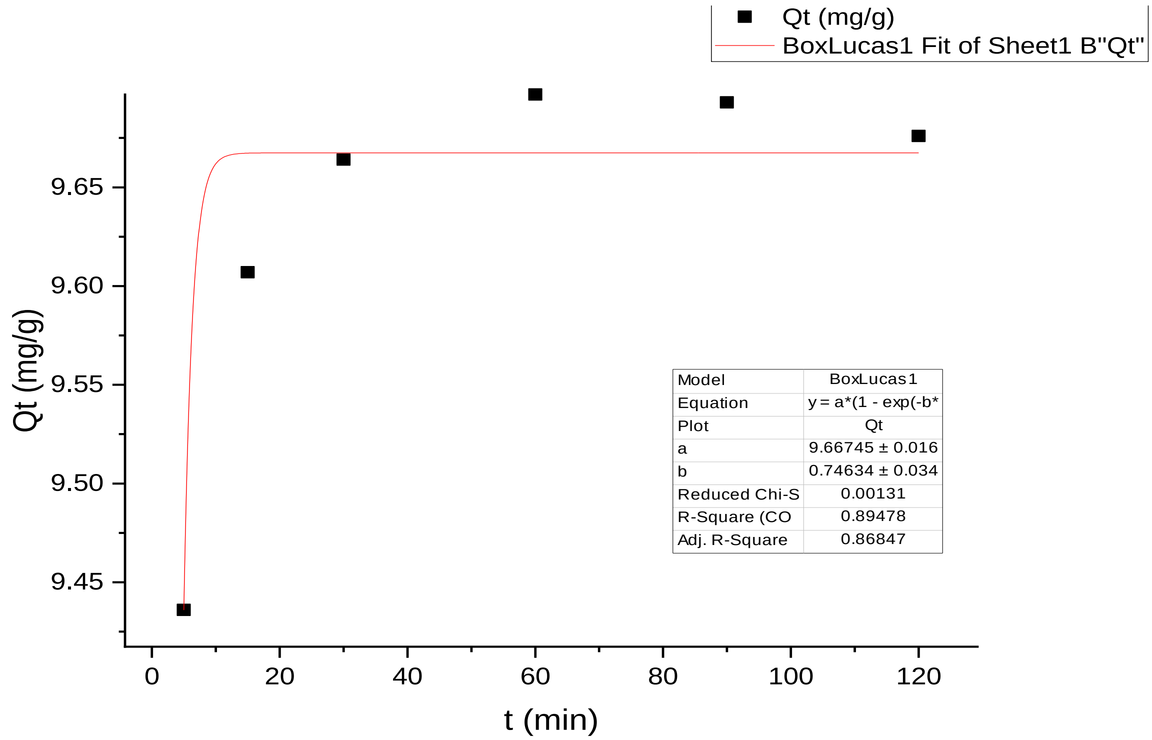

Fig. 14:Pseudo first-orderkinetics plotfor the adsorption of cadmium ion by thebiochar.

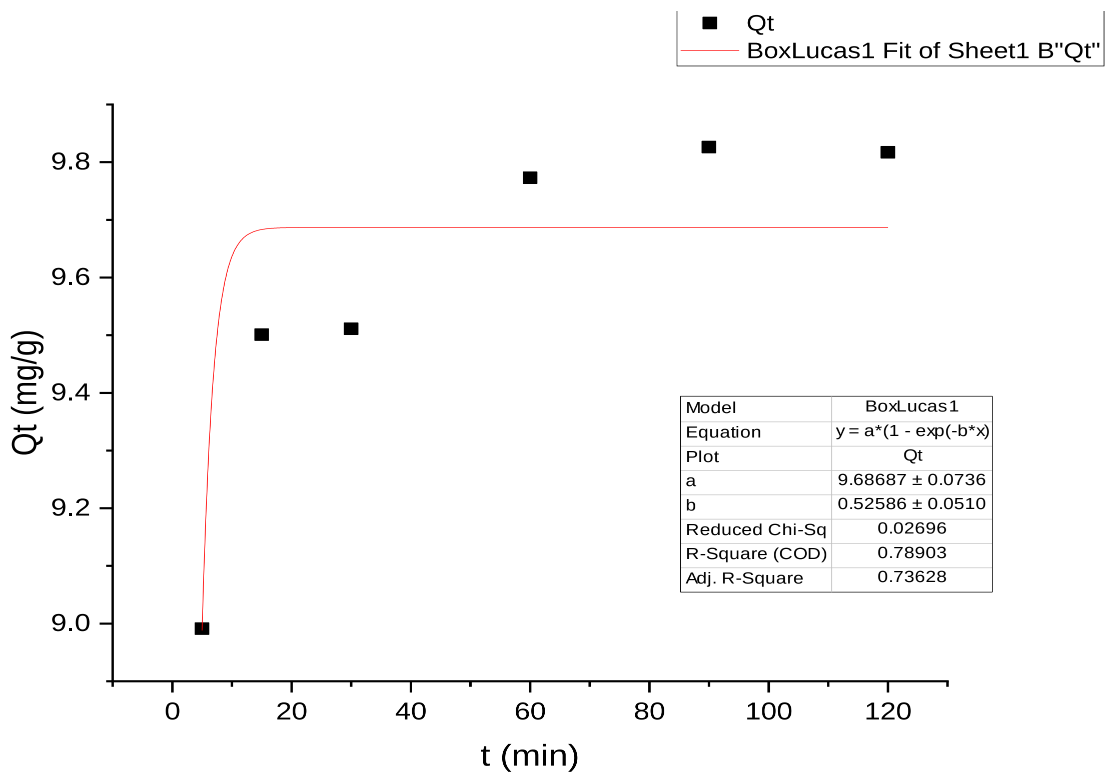

Fig. 15: Pseudo-first-orderkinetics plot for the adsorption ofzinc ion by the biochar

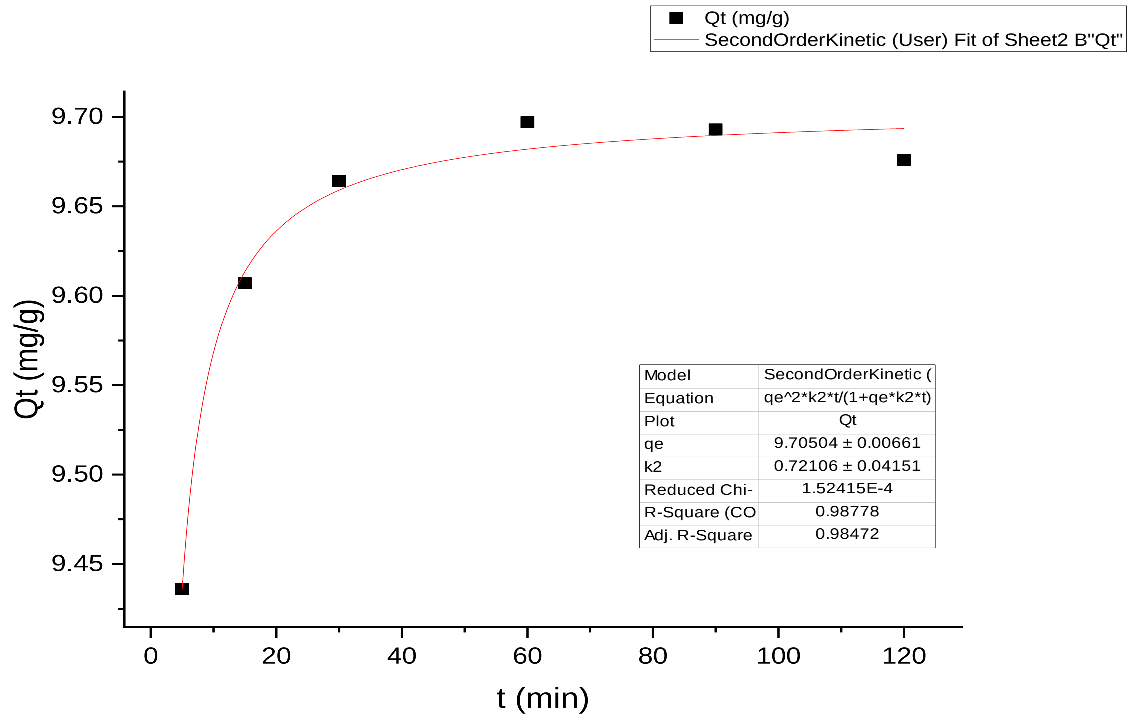

Fig. 16: Pseudo second-order kinetic plots for the adsorption of cadmium ion by the biochar

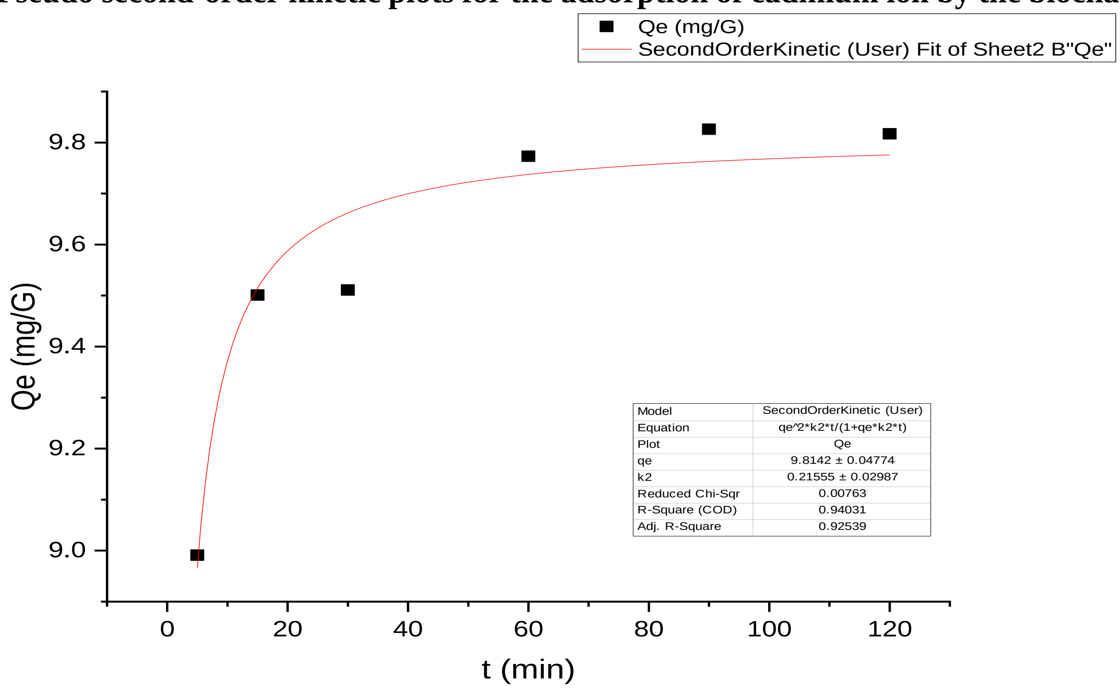

Fig. 17: Pseudo-second-order kinetics plot for the adsorption of zinc ion by the biochar

4.0 Conclusion

Goat horn biochar was produced as a low-cost adsorbent for the adsorption of Cd^{2+} and Zn^{2+} in aqueous solution. The percentage removal of Cd^{2+} and Zn^{2+} increases; as pH increases from 5 to 7 and as initial concentration decreases from 60 to 20 mg/L.Adsorption equilibrium time was at 60 &90 mins and adsorption capacity was 38.844 and 33.692 mg/L for Cd^{2+} and Zn^{2+} respectively.Cadmium ion is better absorbed than zinc ion on the goat horn biochar. The adsorption data best fitted theLangmuir isotherm which indicates a uniform distribution of bonding energy, homogenous and monolayer adsorption of both $Cd^{2+}$and Zn^{2+}.Also,pseudo-second-order best fits the adsorption kinetics, Goat horn biocharmay be an excellent adsorbent for the removal of Cd^{2+} and Zn^{2+} from aqueous solution.

5.0 References

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

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Authors' contributions

Onanuga O. A: Conceptualization, Experimental research, Data analysis and Writing,

Titus M. R: Worked on the experimental design matrix, Data analysis and Statistical interpretation and the results

Bello M. O: Interpretation of the characterized goat horn biochar (FTIR and SEM).

Momoh D. C: Writing, Literature review and Editing of the manuscript.