

# Calcined Corn Cob-Kaolinite Mixture as Adsorbents for the Removal of Heavy Metal from Aqueous Solution

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**Abstract:** This research explores a low-cost composite adsorbent synthesized from calcined corn cobs and kaolinite for the extraction of lead (Pb<sup>2+</sup>) and cadmium (Cd<sup>2+</sup>) from polluted water. Corn cobs were dried and calcined at 150°C, then combined with kaolinite in a 3:2 weight ratio, followed by a thermal treatment at 300°C. The final product, termed Corn Cob-Kaolinite Mixture (CCKM), was tested in batch adsorption studies under different conditions (pH, initial ion concentration, contact time, dosage, and temperature). The adsorption characteristics were modeled using Langmuir and Freundlich isotherms. Results indicated a stronger correlation with the Langmuir model, with R<sup>2</sup> values of 0.914 for Pb<sup>2+</sup> and 0.952 for Cd<sup>2+</sup>, suggesting monolayer adsorption. These findings affirm the effectiveness and affordability of CCKM for treating heavy metal-contaminated water.

**Keywords:** Heavy Metal, Adsorption, Calcined Corncob, Kaolinite.

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## I. INTRODUCTION

The contamination of water sources by heavy metals, primarily from industrial discharges, represents a significant environmental and public health issue. Wastewater from sectors such as metal plating, mining, ceramics, battery manufacturing, and pigment production often contains hazardous metals like chromium, lead, cadmium, nickel, and zinc (Alloway, 2016; Barakat, 2011). These metals can bioaccumulate in living organisms, posing long-term ecological and health risks (Mileusnić et al., 2014). Among various treatment strategies, adsorption has gained prominence for its simplicity and efficiency. Activated carbon, although effective, is prohibitively expensive for widespread use in many developing regions (Crini, 2005).

Consequently, research has increasingly focused on alternative low-cost adsorbents such as agricultural residues, biomass, and natural clays (Ahluwalia & Goyal, 2005). Nigeria possesses abundant clay resources, including kaolinite, which despite its naturally low adsorption capacity, can be enhanced through chemical modification (Bhattacharyya & Gupta, 2006).

Among various remediation techniques, adsorption is preferred for its simplicity and efficacy. However, activated carbon, while efficient, is financially impractical for widespread application in resource-limited settings. Hence, research has turned to economical alternatives such as

agricultural byproducts and natural clays. Nigeria is rich in kaolinite clay, which can be modified to enhance its sorptive capabilities. Combining kaolinite with biomass like corn cobs can significantly boost adsorption capacity due to the increased surface area and availability of active sites.

### ➤ Statement of the Problem

Heavy metal pollution is rising, especially in developing countries like Nigeria. Many conventional remediation methods are expensive or require complex procedures. Thus, there is a pressing need for a cost-effective, efficient approach to removing heavy metals even at low concentrations. Utilizing agricultural waste, such as corn cobs, provides a sustainable and economical solution.

### ➤ Aim of the Study:

This research is aimed at evaluating the absorption potential of calcined corn cobs and kaolinite combo for the removal of heavy metals from tannery industrial wastewater.

### ➤ The objectives of the study:

- Preparation of Calcined Corn Cobs and Kaolinite mixture.
- Characterization of the formed Calcined Corn Cob-Kaolinite mixture
- To determine the sorptivebehaviour of the Calcined Corn Cobs and Kaolinite mixture for the removal of Cu(II), Zn(II), and Pb(II).
- To establish the adsorption isotherm using Freundlich and Langmuir Isotherm equations.

### ➤ *Scope of the Study*

The scope of this research work will focus on the use of Calcined Corn Cobs And Kaolinite Combo produced from corn and kaolinite for the adsorption of heavy metals from effluents water. Adsorption of heavy metals Cu(II), Zn(II), and Pb(II) will be investigated only.

### ➤ *Significance of the Study*

Heavy metals are non-biodegradable and undergo a global eco-biological cycle in which natural waters remain one of its main pathways (Lenntech, 2013). Corn cobs and Kaolinite are readily available waste/natural materials and have the potential to give a cheap route for the removal of heavy metals from effluent waters. Its affordability and modification will aid regeneration and environmental friendliness which would help save the costs of remediation of heavy metals Cu(II), Zn(II), and Pb(II) commonly associated with wastewaters. These metals are known to be toxic and possess the capacity to affect aquatic organisms and become components of the food chain, thereby affecting human beings who may use water directly or indirectly (Nwankwoala & Ememu, 2018).

## II. LITERATURE REVIEW

Technological advancements have significantly contributed to environmental degradation, with industrial effluents being a major source of water pollution (Adelekan & Abegunde, 2011). Trace metals such as cadmium, lead, zinc, copper, and chromium, often found in industrial wastewater, pose serious health risks when discharged into the environment without adequate treatment (Barakat, 2011). These metals, being non-biodegradable, accumulate in the ecosystem and enter food chains (Alloway, 2016).

Among various treatment methods, adsorption stands out for its cost-effectiveness and operational simplicity (Crini, 2005). While activated carbon remains a gold standard, its high cost has led to research into alternative adsorbents like agricultural waste (e.g., coconut husk, sawdust, maize cob) and natural clays (Ahluwalia & Goyal, 2005; Davis et al., 2000). The combination of adsorbents has shown enhanced metal removal efficiency (Unuabonah et al., 2008).

Maize cobs have demonstrated high sorption potential, particularly for lead ions, and are abundantly available in Nigeria (Nwadiogbu et al., 2014). Kaolinite, a natural clay, though less efficient on its own, can be modified with biomass to improve its adsorption capacity (Bhattacharyya & Gupta, 2006). The use of such composites not only promotes environmental sustainability but also reduces waste and water treatment costs (Akpomie & Dawodu, 2015).

### ➤ *Materials*

The materials employed in this research includes: corn cobs, kaolinite, heavy metals (lead (II) and cadmium (II) salts), deionized water, distilled water,

### ➤ *Method Sample Collection*

Maize cobs samples were collected from a local farmer in Massaka in Karu local govt. Nasarawa. The maize cobs were

moved to the laboratory where they were washed with distilled water and sun dried.

### ➤ *Sample Preparation*

The dry maize cobs were heated in furnace in absence of air at a temperature of 150°C for eight hours. The dried cob obtained was cooled in air and crushed to finer particles using motor and pestle.

### ➤ *Production of Calcined Corn Cob and Kaolinite mixture:*

Kaolinite and the corn-cob were mixed in the ratio of 3:2 respectively (Based on mass). The mixture was then heated in the furnace at a temperature of 350°C for six hours after which it was cooled in air stored in stoppered beaker ready for use.

### ➤ *Removal Efficiency of Produced corn cobs for heavy metal Removal*

#### • *Optimization of contact time*

To determine equilibrium time for both lead (II) and cadmium (II) ions batch experiments for both were carried out using the adsorbent. 0.5g of the adsorbent was mixed with 100mL solution of both lead and cadmium ions at initial concentration of 100 mg/L. The mixture was then shaken constantly at time intervals of 10 minutes for 50 minutes.

In order to get maximum adsorption a mixture of 0.5g of the adsorbent and 100mL of both lead and cadmium was shaken at constant speed for 50 minutes. After completion of each batch experiment the mixture was centrifuged at a speed of 3800rpm for 10 minutes and then decanted. Absorbance's of lead (II) and cadmium (II) ions in the remaining solutions was determined using AAS.

#### • *Optimization of initial metal ion concentration*

The initial metal ion concentration for both lead (II) and cadmium (II) ions were varied from 20 to 100 mg/L. 0.5g of the adsorbent was added to 100mL of the solution at different concentrations as stated above, the mixture was then shaken at a constant speed for two hours after which it was centrifuged for 20 minutes at 3800rpm and filtered. The filtrate was analyzed for the remaining metal ion concentration using AAS.

#### • *Optimization of temperature*

0.5g of the adsorbents were added to 10 mg/L of 50mL of both lead (II) and cadmium (II) ions solution, the mixture was then shaken at a constant speed for two hours at different temperatures of 27, 32, 37, 42 47 and 52°C after which it was centrifuged for 20 minutes at 3800rpm and then filtered. The filtrate was analysed for the remaining metal ions concentrations using AAS.

#### • *Optimization of adsorbent dose*

Effect of adsorbent dose on adsorption of metal ions was achieved by varying the adsorbent dose from 0.5 to 2.5g for all the adsorbents. 600ppm solution was used for both metal ions. The mixture was shaken at a constant shaking speed for two hours after which it was centrifuged and filtered; the filtrate was analysed for the remaining metal ions concentrations using AAS.

### • Optimization of pH

The influence of pH on the adsorption efficiency of lead and cadmium ions was assessed using solutions maintained at pH 7. Prior research indicates that optimal adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  typically occurs within the pH range of 6 to 9 (Mbugua et al., 2014). To regulate the pH, a calibrated pH meter—standardized with buffer solutions of pH 3, 5, 7, 10, and 12—was employed. Adjustments were made using concentrated nitric acid ( $HNO_3$ ) and sodium hydroxide (NaOH) solutions.

In this study, equilibrium adsorption isotherms were utilized to describe the interaction between metal ions and the surface of the adsorbent under constant temperature conditions. An adsorption isotherm graphically represents the relationship between the amount of solute adsorbed per unit mass of adsorbent ( $q_e$ ) and its equilibrium concentration in solution ( $C_e$ ). These isotherms are essential for understanding surface coverage and adsorption capacity. The equilibrium data will be interpreted using the Langmuir and Freundlich models, which provide insight into adsorption mechanisms and surface characteristics (Foo & Hameed, 2010).

### ➤ Langmuir adsorption isotherm

Langmuir equation is represented in its linearized form as shown below

$$\frac{1}{q_e} = \frac{1}{q_m K_L} C_e + \frac{1}{q_m} \quad (3.6)$$

In this equation Plot of  $1/q_e$  vs  $1/C_e$  gives the constants  $K_L$  and  $q_m$  from the slope and the intercept respectively

### ➤ Generalized form is given explicitly by

$$q_e = \frac{q_m K_L}{1 + K_L C_e} \quad (3.7)$$

## III. DATA PRESENTATION AND ANALYSIS

### ➤ Data Presentation

The result of the chemical properties of the formed corn cob mixture with kaolinate is given in figure 4.1.1 through to 4.1.3,

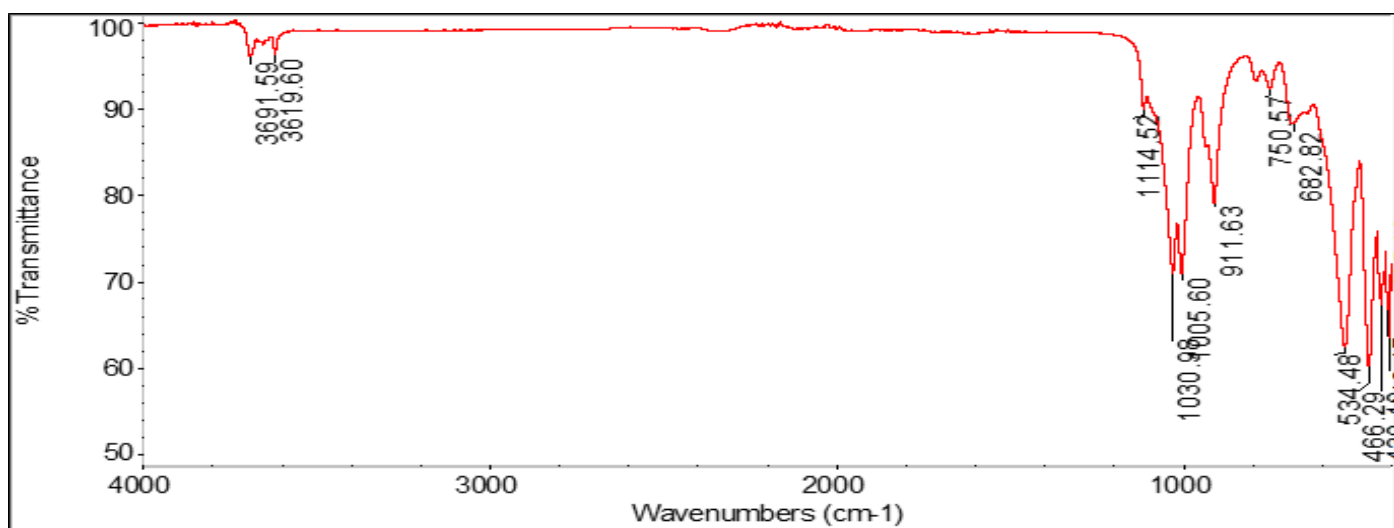


Fig 1 (Corn cob)

Where  $K_L$  ( $Lmol/dm^3$ ) is the Langmuir equilibrium constant,  $q_e$  ( $molg^{-1}$ ) and  $C_e$  ( $mol/dm^3$ ) are the amount of biosorbed metals per unit weight of biosorbent and residual  $Pb(II)$ ,  $Cr(II)$ ,  $Cd(II)$ ,  $Cu(II)$  and  $Zn(II)$  concentration at equilibrium respectively and  $q_m$  is the maximum amount of  $Pb(II)$  per unit weight of biosorbent to form a complete monolayer on the surface. A high  $K_L$  value indicates a high affinity for the binding of  $Pb(II)$ ,  $Cr(II)$ ,  $Cd(II)$ ,  $Cu(II)$  and  $Zn(II)$  ions. A plot of  $1/q_e$  against  $1/C_e$  gives the constants  $K_L$  and  $q_e$  from the slope and the intercept respectively (Lawal, Sanni, Ajayi, & Rabi, 2010; Putra et al., 2014).

### ➤ Freundlich adsorption Isotherm

Freundlich isotherm model assumes a non-ideal adsorption on heterogeneous surfaces in a multilayer coverage which suggests that stronger binding sites are occupied first, followed by weaker binding sites. In order words, as the degree of site occupation increases, the binding strength decreases (Jamhour, Ababneh, & Alrawasdeh, 2016).

Freundlich model with the linear plotted  $\log q_e$  versus  $\log C_e$  shown in the following equation  $\log q_e = \log K_f + \frac{1}{n} \log C_e$ . The equation was adopted from Wang et al. (2016), where  $K_f$  is Freundlich Constant and is roughly an indicator of the adsorption capacity ( $mg/g$ ),  $n$  is Freundlich Coefficient,  $C_e$  is the equilibrium concentration in ( $mg/L$ ) and  $K_f$  and  $n$  are determine by plotting a graph of  $q_e$  against  $C_e$ .

The linear form of Freundlich expression will yield the constant  $K_f$  and  $1/n$ . Written in the generalized form as

$$q_e = K_f C_e^{1/n} \quad (3.9)$$

Plot of against  $\log q_e$  vs.  $\log C_e$  gives the constants  $1/n$  and  $K_f$  from the slope and intercept respectively (Jamhouret al., 2016; Kord, Bazrafshan, Farzadkia, & Amimi, 2013).

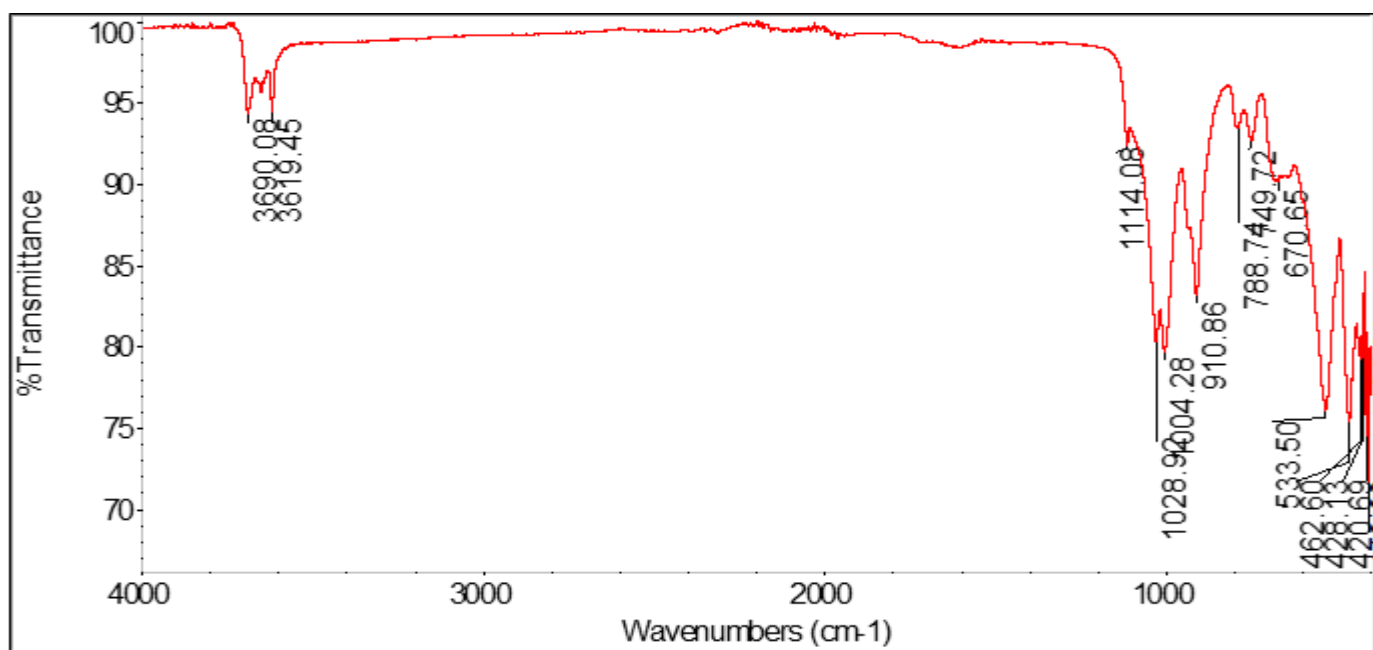


Fig 2 (Kaolinite)

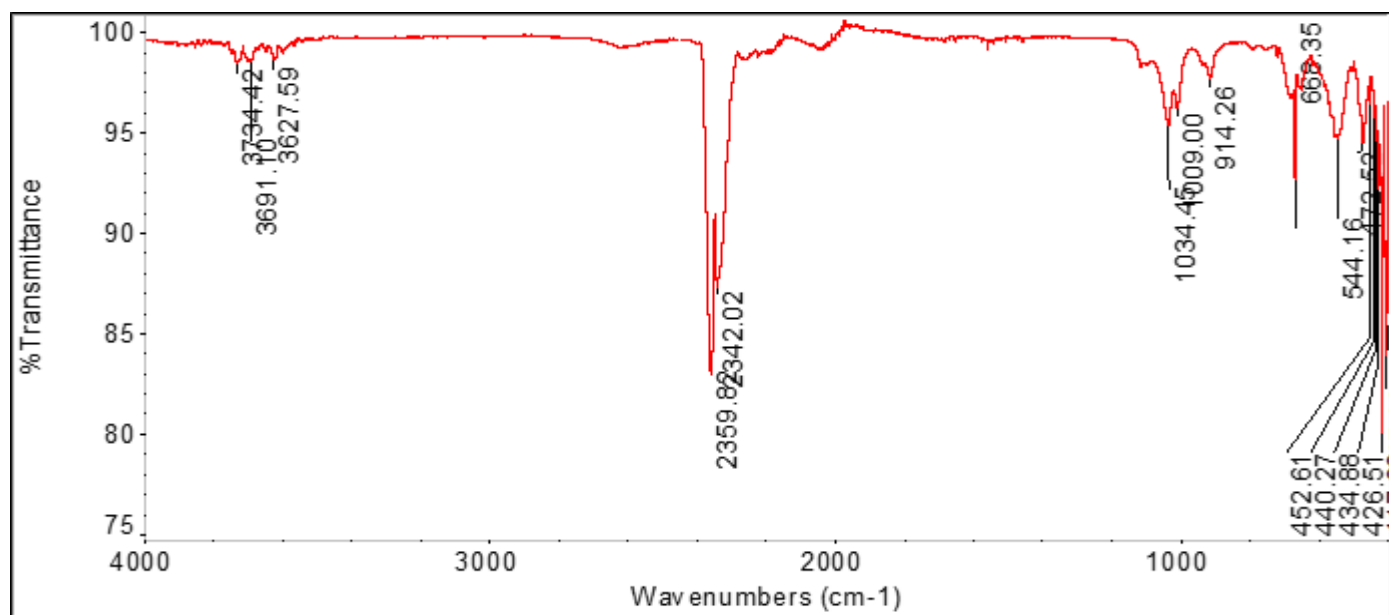


Fig 3 (Corn cob and Kaolinite mixture)

Table 1 Effect of pH on Adsorption rate-  $\text{Cd}^{2+}$ 

pH	Equilibrium Conc $C_{eq}$ mg/L	Amount Adsorbed $C_t$ mg/L	% Adsorption
3	99.40	0.60	0.60
5	99.68	0.32	0.32
7	99.05	0.95	0.95
10	50.75	49.25	49.25
12	7.26	92.74	92.74

Table 2 Effect of pH on Adsorption rate-  $\text{Pb}^{2+}$ 

pH	Equilibrium Conc $C_{eq}$ mg/L	Amount Adsorbed $C_t$ mg/L	% Adsorption
3	99.18	0.82	0.82
5	95.60	4.40	4.40
7	48.02	51.98	51.98
10	25.73	74.27	74.27
12	9.04	90.96	90.96

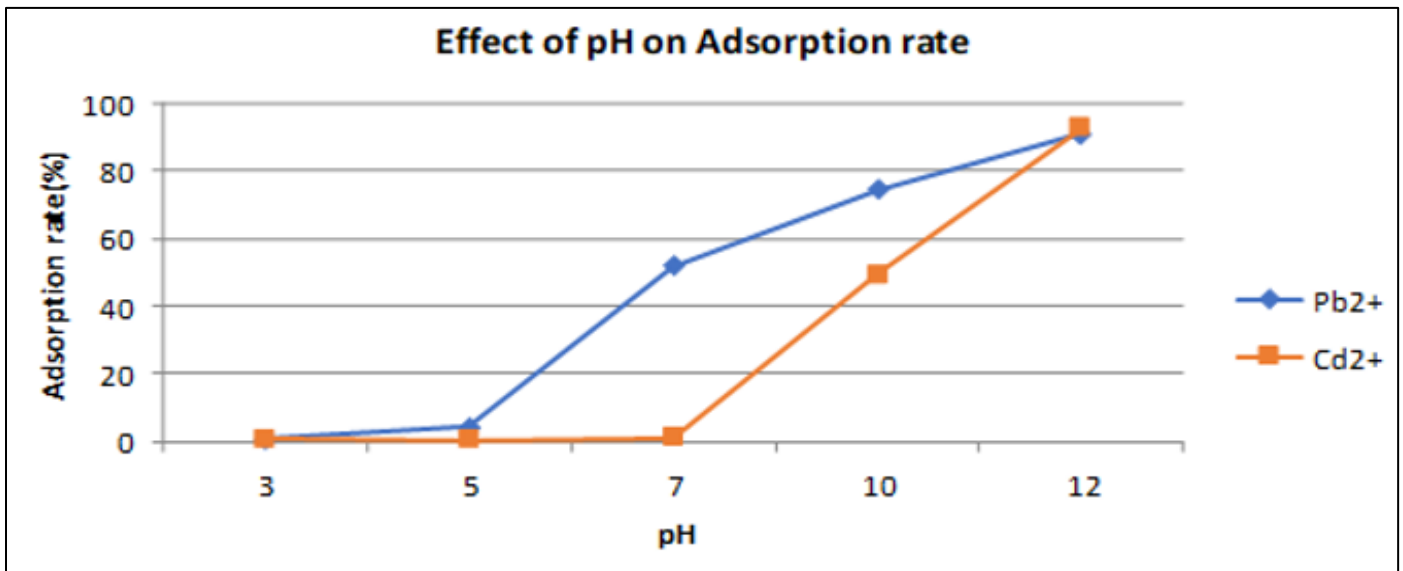


Fig 4 Effect of pH on percentage removal of metal ions

Table 3 Effect of Concentration on Adsorption rate-Cd<sup>2+</sup>

Initial conc. (mg/l)	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
20	18.38	1.62	8.10
40	36.30	3.70	9.26
60	53.27	6.76	11.27
80	68.14	11.86	14.83
100	74.75	25.25	25.25

Table 4 Effect of Concentration on Adsorption rate-Pb<sup>2+</sup>

Initial conc. (mg/l)	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
20	4.68	15.32	76.60
40	12.63	27.37	68.43
60	15.96	44.04	73.40
80	16.61	63.39	78.75
100	22.01	77.99	77.99

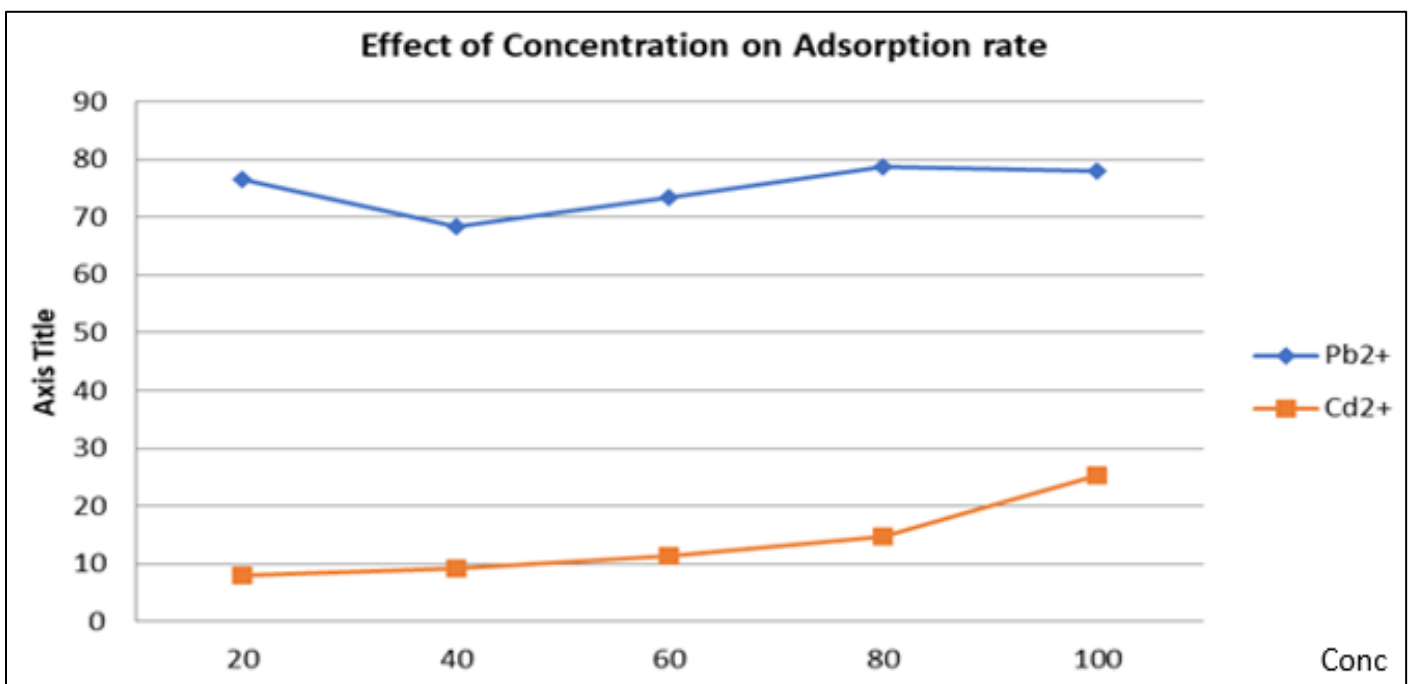


Fig 5 Effect of initial metal concentration on percentage removal of lead (II) ions (0.5 g, 25°C, 2 hrs, 240 rpm and pH 7)

Table 5 Effect of adsorbent dose on Adsorption rate-Cd<sup>2+</sup>

Adsorbent dose	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
0.5	96.01	3.99	3.99
1.0	96.12	3.88	3.88
1.5	95.42	4.58	4.58
2.0	95.59	4.41	4.41
2.5	95.22	4.78	4.78

Table 6 Effect of adsorbent dose on Adsorption rate-Pb<sup>2+</sup>

Adsorbent dose	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
0.5	90.88	9.12	9.12
1.0	87.78	12.22	12.22
1.5	80.14	19.86	19.86
2.0	76.90	23.10	23.10
2.5	68.10	31.90	31.90

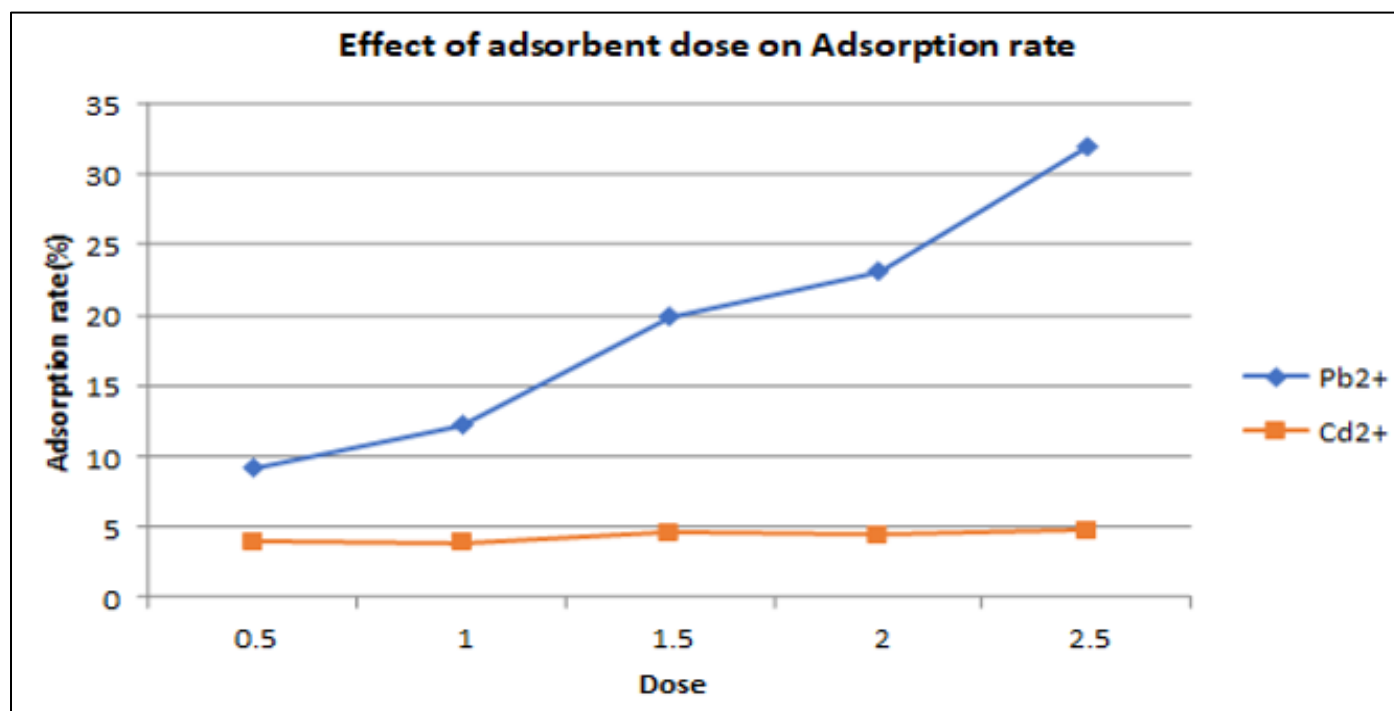


Fig 6 Effect of adsorbent dose on percentage removal of cadmium (II) ions (25°C, 100 mg/L, 2 hrs, 240 rpm and pH 7)

Table 7 Effect of Contact Time on Adsorption rate-Cd<sup>2+</sup>

Contact Time mins	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
0	100	0	0
15	99.12	0.88	0.88
30	98.95	1.05	1.05
45	98.47	1.53	1.53
60	98.12	1.88	1.88
75	97.95	2.05	2.05

Table 8 Effect of Contact Time on Adsorption rate-Pb<sup>2+</sup>

Contact Time Mins	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
0	100	0	0
15	91.32	8.68	8.68
30	90.68	9.32	9.32
45	83.11	16.89	16.89
60	82.06	17.94	17.94
75	81.17	18.83	18.83



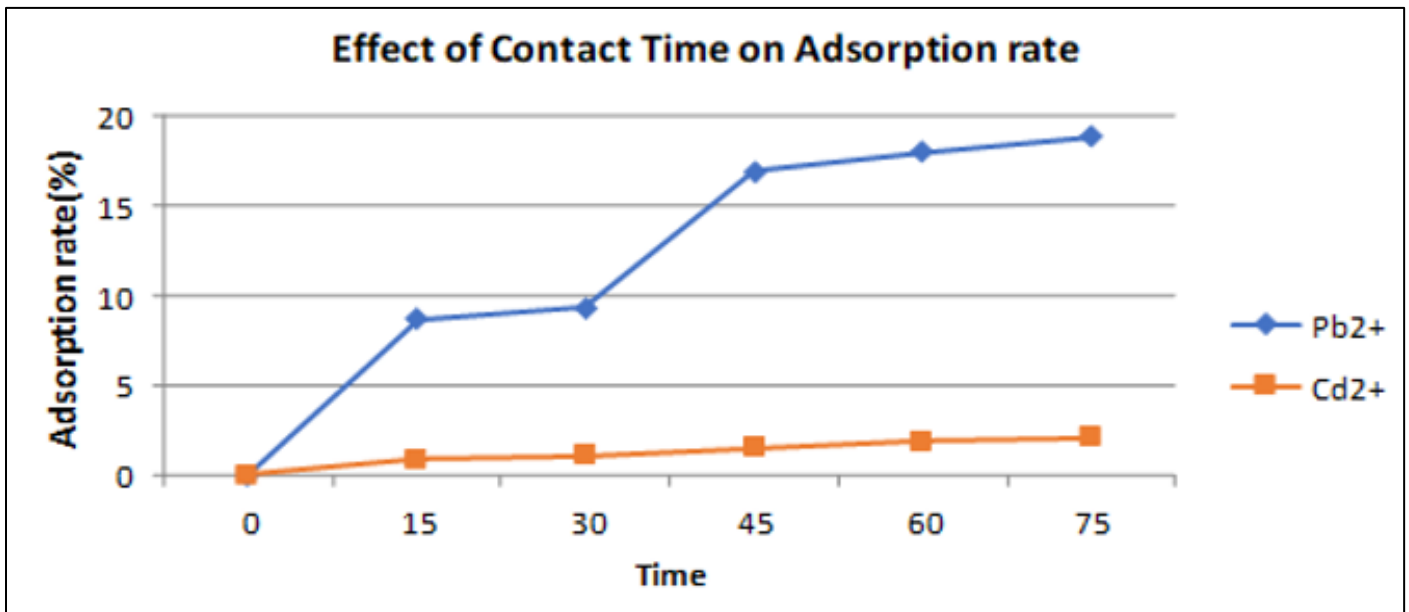


Fig 7 Effect of contact time on percentage removal of cadmium (II) ions (0.5g, 25°C, 100 mg/L, 240 rpm and pH 7)

Table 9 Effect of Temperature on Adsorption rate-Cd<sup>2+</sup>

Temperature celcius	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
15	96.31	3.69	3.69
30	96.21	3.79	3.79
45	96.52	3.48	3.48
60	95.83	4.17	4.17
75	96.58	3.42	3.42

Table 10 Effect of Temperature on Adsorption rate-Pb<sup>2+</sup>

Temperature celcius	Equilibrium conc C <sub>eq</sub> mg/l	Amount Adsorbed C <sub>t</sub> mg/l	%Adsorption
15	87.68	12.32	12.32
30	83.57	16.43	16.43
45	86.10	13.90	13.90
60	84.83	15.17	15.17
75	85.19	14.81	14.81

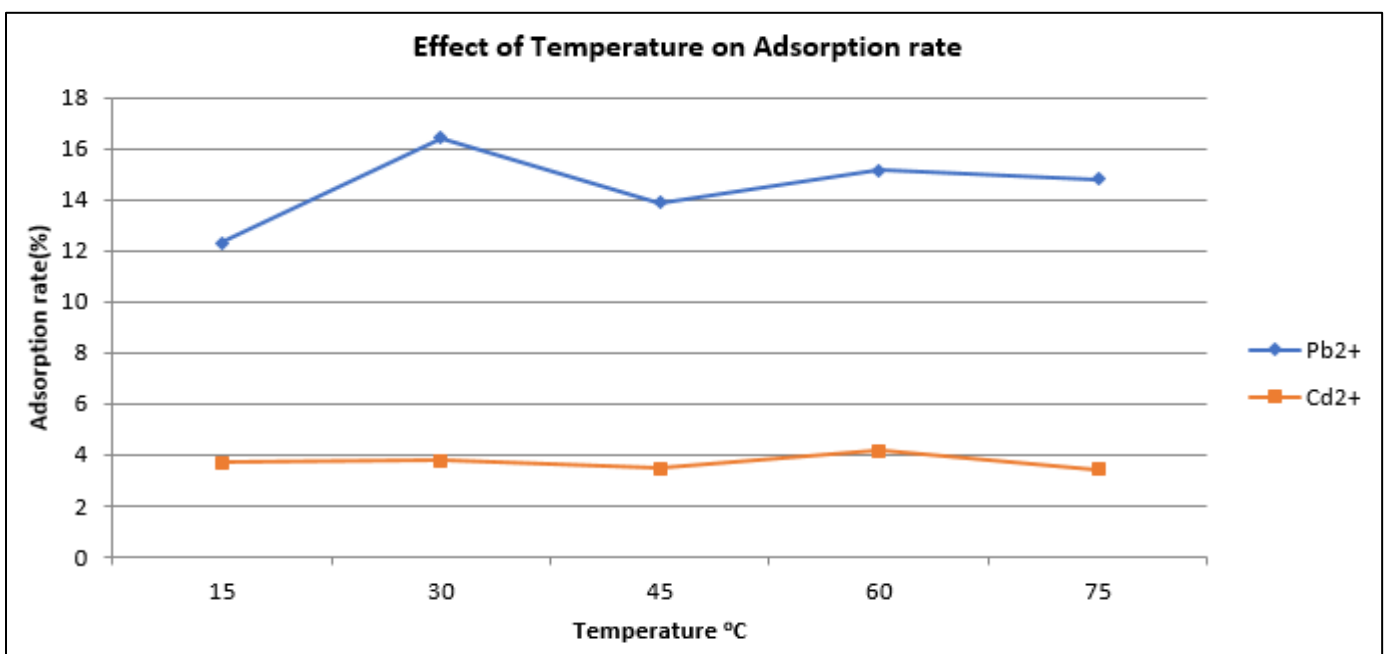


Fig 8 Effect of temperature on percentage removal of lead (II) ions (0.5 g, 100 mg/L, 2hrs 240rpm and pH 7)

Table 11 Cadmium

$C_i$	$C_e$	$q_e$	$\text{Log } q_e$	$\text{Log } C_e$	$C_e/q_e$
20	18.38	324	2.511	1.264	0.057
40	36.30	740	2.869	1.560	0.049
60	53.27	1352	3.131	1.727	0.040
80	63.14	2372	3.375	1.800	0.027
100	74.75	14950	4.175	1.874	0.005

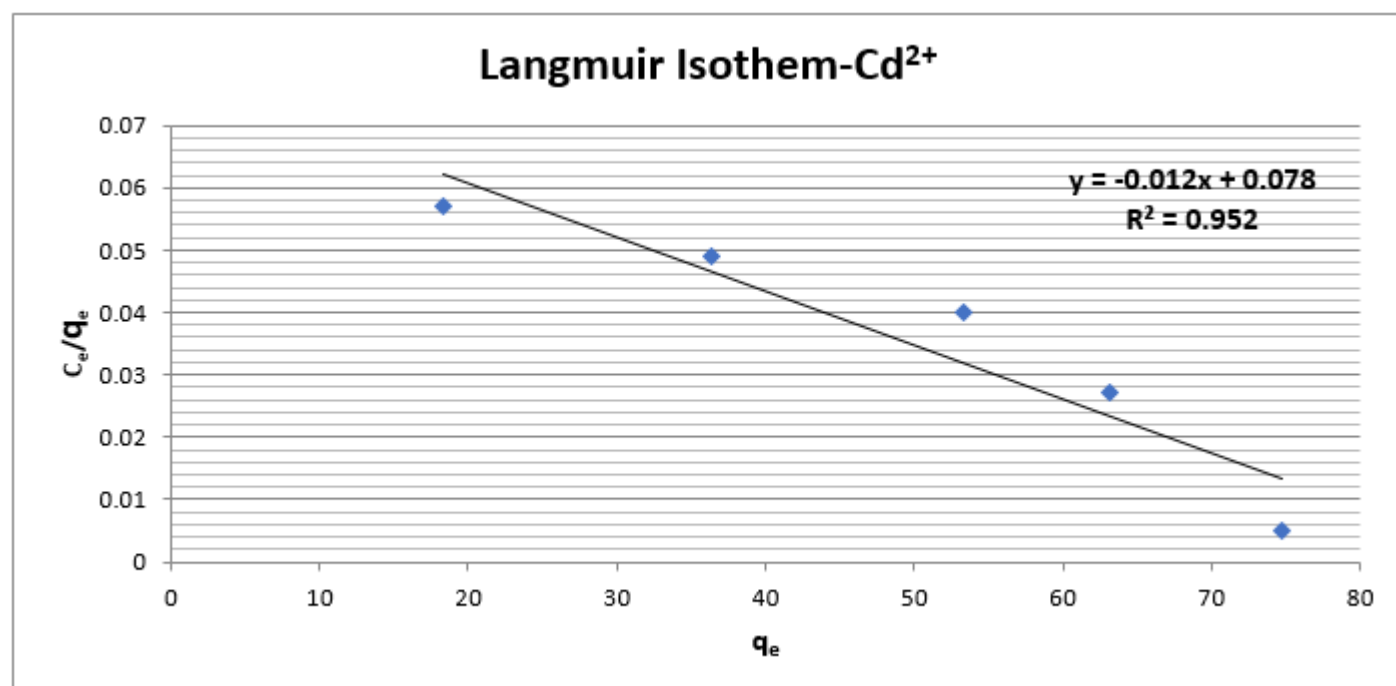
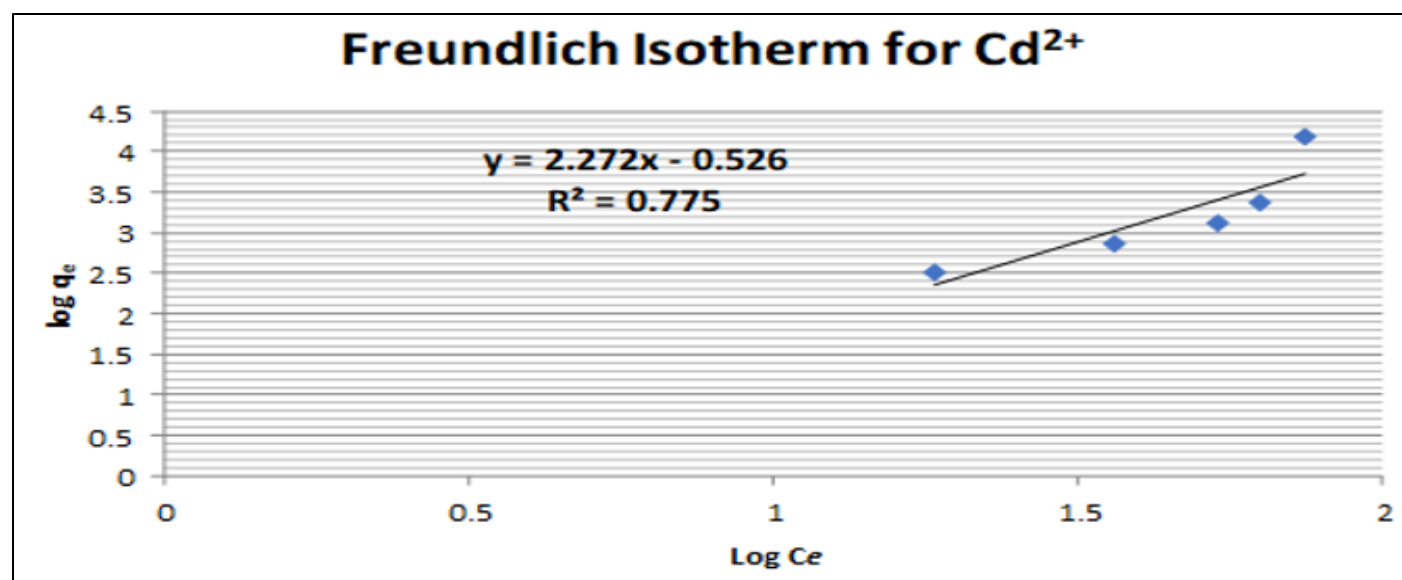
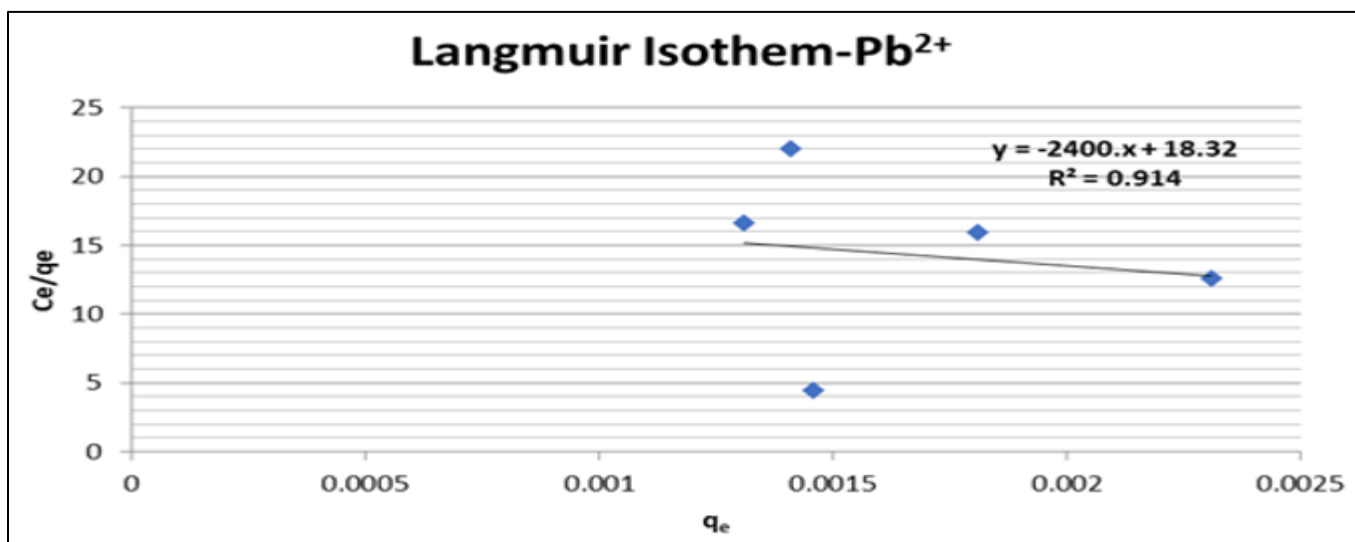
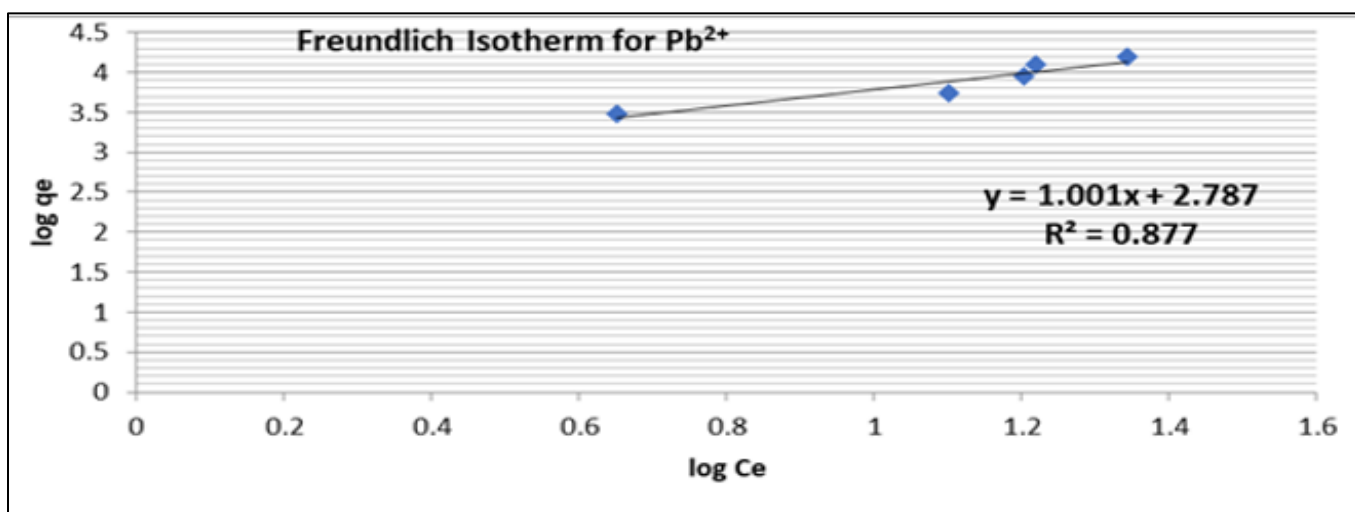
Fig 9 Langmuir isotherm for  $\text{Cd}^{2+}$ Fig10 Freundlich isotherm for  $\text{Cd}^{2+}$ 

Table 12 Lead

$C_i$	$C_e$	$q_e$	$\text{Log } q_e$	$\text{Log } C_e$	$C_e/q_e$
20	4.48	3064	3.486	0.651	0.00146
40	12.63	5474	3.738	1.101	0.00231
60	15.96	8808	3.945	1.203	0.00181
80	16.61	12678	4.103	1.220	0.00131
100	22.01	15598	4.193	1.343	0.00141



Fig 11 Langmuir isotherm for Pb<sup>2+</sup>Fig 12 Freundlich isotherm for Pb<sup>2+</sup>

#### ➤ Analysis

The influence of various operational parameters—such as adsorbent dosage, contact time, initial metal ion concentration, agitation speed, and temperature—on the removal efficiency of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions was systematically evaluated by altering one parameter at a time while keeping the others fixed. The residual metal ion concentrations were then measured to assess adsorption performance. All experiments were carried out at pH 7, except where pH was intentionally varied to study its effect (Mbugua et al., 2014).

#### ➤ Characterization of Adsorbents:

The adsorbents were characterized using Fourier Transform Infrared Spectroscopy (FTIR) to identify functional groups involved in heavy metal adsorption. FTIR spectra of kaolinite, maize cob, and their composite revealed significant functional bands associated with hydroxyl, carboxyl, and silicate groups. Shifts and intensity changes in bands following thermal treatment and combination indicated successful composite formation and the presence of active sites capable of binding metal ions (Unuabonah et al., 2008).

#### ➤ Effect of pH:

The adsorption of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions was highly influenced by the pH of the solution. Maximum adsorption occurred in the pH range of 6 to 9. At lower pH values, competition between H<sup>+</sup> and metal ions limited adsorption, while higher pH values led to possible metal precipitation. The composite showed optimal performance at pH 7–8 for both ions (Mbugua et al., 2014).

#### ➤ Initial Metal Concentration:

Increasing the initial concentration of Pb<sup>2+</sup> led to a rise in adsorption percentage up to a saturation point. For Cd<sup>2+</sup>, the removal efficiency was relatively lower and increased modestly with concentration. The difference in performance suggests varying affinities of the composite for the two metal ions (Nwadiogbu et al., 2014).

#### ➤ Adsorbent Dosage:

A higher dosage of the composite material improved Pb<sup>2+</sup> removal due to increased surface area and availability of binding sites. However, the change in adsorption for Cd<sup>2+</sup> remained marginal, implying possible saturation or lower binding affinity (Davis et al., 2000).

➤ *Contact Time:*

Equilibrium was reached within 60 minutes for both metals.  $Pb^{2+}$  adsorption increased significantly with time before stabilizing, whereas  $Cd^{2+}$  adsorption followed a slower and more linear trend (Crini, 2005).

➤ *Temperature Effect:*

Adsorption efficiency for both  $Pb^{2+}$  and  $Cd^{2+}$  decreased with increasing temperature, suggesting that the process is exothermic. Lower temperatures favored binding, likely due to reduced kinetic energy and stronger interactions between adsorbate and adsorbent (Mbugua et al., 2014; Barakat, 2011).

➤ *Adsorption Isotherms:*

The Langmuir and Freundlich models were applied to interpret the experimental data.  $Pb^{2+}$  showed a good fit to both models, indicating monolayer and heterogeneous adsorption behaviors.  $Cd^{2+}$  adsorption aligned more closely with the Langmuir model, suggesting uniform surface interaction. The higher correlation coefficients for Langmuir indicate its better predictive capability in this study (Bhattacharyya & Gupta, 2006; Akpomie & Dawodu, 2015).

#### IV. CONCLUSION

Findings herein show that KCM is effective in removing lead ions, cadmium ions from contaminated water. The efficiency of the KCM adsorbent to remove  **$Cd^{2+}$  and  $Pb^{2+}$  from water is affected by initial metal ion concentration, temperature, contact time, and adsorbent dose** (this was not significant for  $Cd^{2+}$ ). The sorption studies for cadmium ions showed that the isotherms fitted in Langmuir model. The sorption studies for lead ions gave best fit in Langmuir model, it also had good fit in Freundlich model.

#### RECOMMENDATIONS

For further studies the following are recommended.

- Investigate effects of chemical activation on adsorbent performance.
- Optimize calcination parameters for improved efficacy.
- Explore other biomass-kaolinite ratios for additional heavy metals.

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