



## COMPARATIVE STUDY OF THE BIOREMEDIATION OF CADMIUM FROM INDUSTRIAL EFFLUENT BY MELON HUSK MODIFIED WITH SULPHURIC ACID AND SODIUM HYDROXIDE



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### ABSTRACT

Melon husk, a readily available agricultural waste product was used as a low-cost potential adsorbent to remove cadmium and from industrial effluents. Adsorption studies were carried out on two different activated melon husks as a function of parameters such as contact time, adsorbent dosage and adsorbate concentration. Cadmium removal was found to be dependent on the three parameters with maximum removal attained at 50 min with 1.0g for sodium hydroxide (NaOH) activated melon husks and at 70 min with 0.6 g for sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) activated melon husk. The metal was mostly removed at low adsorbate concentration. Adsorption isotherms correlated well with both Langmuir and Freundlich isotherm models and their R<sup>2</sup> values are 1 for both. Experimental data were also evaluated to find out kinetic characteristics of the adsorption process. Adsorption process for the target heavy metal ion was found to follow pseudo-second order adsorption kinetics. While their r<sup>2</sup> values are 0.7979 and 0.8486 for both H<sub>2</sub>SO<sub>4</sub> and NaOH modified melon husks. The r<sup>2</sup> values showed that both H<sub>2</sub>SO<sub>4</sub> and NaOH modified melon husks are efficient adsorbents with NaOH more efficient. Activated melon husk, a readily available adsorbent was found to be efficient in the uptake of Cd(II) ions in industrial effluents, thus, making it an excellent alternative for the removal of heavy metals from water and waste water.

**Keywords:** Adsorbent, Bioadsorption, Effluent, Melon husk, Sulphuric acid, sodium hydroxide, cadmium

### INTRODUCTION

Contamination of the environment; land, atmosphere and water which include streams, lakes, underground water, bays, or oceans by substances harmful to living things has become a serious issue of concern. The contamination of water seems to be more serious due to the place and importance of water to life. Water is necessary to life on earth. All organisms contain it; some live in it; some consume it. Plants and animals require water that is moderately pure and they cannot survive if their water is loaded with toxic chemicals or harmful microorganisms. If severe, water pollution can kill large numbers of fish, birds, and other animals in some cases killing all members of a species in an affected area.

Industrial effluents are one of the major causes of environmental pollutions. Effluent discharged from dyeing industries are highly coloured, of low biological oxygen demand (BOD) and high chemical oxygen demand (COD). Disposal of this coloured water into receiving waters can be toxic to aquatic life [2]. They also pose a problem because they may be mutagenic and carcinogenic [3] and can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver, brain and central nervous system [4].

Industrial activities like mining, painting, car manufacturing, metal plating, tanneries and

agricultural activities like intensive use of fertilizers and fungicides are the main sources of wastes containing heavy metals. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous even at low concentrations. Heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), Chromium (Cr), Thallium (Tl) and Lead (Pb) [5]. Among these toxic heavy metals, mercury, lead and cadmium have been called “the big three” and are in the lime light due to their major impact on the environment [6, 7].

Heavy metals are considered to be one of the most hazardous water contaminants. According to the World Health Organization [8] among the most toxic heavy metals are cadmium, chromium, copper, lead, mercury and nickel. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the concentration in the environment. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater [1].

The discharge of these waste containing heavy metals

and other discharges which includes plastic wastes, such as polyethylene terephthalate (PET) and Polyvinyl Chloride (PVC), industrial wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewages, sludge, fertilizers etc, constitutes a serious challenge in waste management strategies. It is therefore of main relevance to find alternatives by which such materials can be handled in a more environmentally friendly or acceptable procedures [9].

Many conventional methods such as chemical precipitation, chemical coagulation, chemical oxidation and biological techniques, solidification, electrolytic recovery, ion exchange have been used for removal of dyes and metal ions. The application of such method however, is sometimes restricted because of technical or economical constraints, [10, 11]. Hence, more economical means such as biosorption for the removal of metals have been sought for. It is non-polluting, and it can be highly selective, more efficient, easy to operate and hence cost effective. Also, adsorption using activated carbon have been reported [12,]. The removal of heavy metals by Activated carbon (AC) is economically favourable and technically easy [13]. Other advantage of AC over other methods of remediation of heavy metals from waste water is that, it is sludge-free. ACs, therefore, are widely used to treat waters contaminated with heavy metals.

The use of such non-conventional wastes as carbon source for the production of AC might be an efficient alternative for both, adoption of effective waste management practice, and production of low-cost AC. Plastic wastes, various industrial wastes like fly ashes, pitch, polymer residues, sawdust [14, 15], old newspaper, tires and sewage sludge have been raw materials for AC production. Several agricultural wastes products have also been found useful in AC production, like coconut shell, rice husk, groundnut husk, cassava peel, maize cob [16], banana pith, *Medicago sativa* (Alfalfa), sphagnum, moss peat, sunflower stalks, fungal, bacteria, algae [17,18,19] and others.

Commercially available activated carbons are expensive. In a developing economy like Nigeria, it is better to find low-cost adsorbent to be used in this field. There is therefore, a need to search for an effective adsorbent for environmentally friendly and economically waste water treatment. This work therefore focuses on the use of activated carbon (AC) from melon (*Citrullus colocynthis*) husk as low-cost adsorbent materials for the removal of cadmium and lead from waste water that is discharged into water bodies. The objective of the study is to convert the waste melon husk into usable material and use same in effecting the treatment of the industrial effluents

containing cadmium and lead. The study also aims to assess the efficiency of waste melon husk as an environmentally friendly material for metal remediation.

## MATERIALS AND METHODS

### [1] *Collection of Adsorbent*

The melon husks were collected from the melon sellers at the local market in Ogbomoso town of Oyo State, Nigeria.

### [2] *Preparation of Adsorbent*

[3] Debris and stones were separated from the melon husks by hand-picking. The husks were washed thoroughly with tap water and rinsed with distilled water before being sun-dried. The husks were grounded at the market using the miller's machine. The ground husks were sieved with ordinary kitchen sieve to achieve a more uniform particle size. The husk was now ready for modification.

### [4] *Modification with Concentrated H<sub>2</sub>SO<sub>4</sub>*

The ground husk was treated with H<sub>2</sub>SO<sub>4</sub>, and was dried. It was then washed with distilled water, after which it was soaked in 1% NaHCO<sub>3</sub> overnight to remove residual acid. It was oven-dried at 150°C for 24 hours. The activated husk was then ground further and sieved particle size of 250-500µm was collected and stored in an air-tight container for use [20,21] modification method.

### *Modification with NaOH*

The ground husk was soaked in 0.5m NaOH for 12 hours. It was washed with distilled water to remove excess NaOH and was soaked in 1% formaldehyde at 50°C for 4 hours to prevent any further colour interference during activation. It was rinsed to remove free HCHO (formaldehyde) and was now dried at 60°C for 2 hours. It was further ground and sieved and 500µm particle size was selected. This was to provide a larger surface area for adsorption. The NaOH activated melon husk was stored in an air-tight container ready for use. [21,22].

### [5] *Adsorption procedure*

The modified melon husks were used to treat Cadmium (II) simulated waste water. The equilibrium time (contact time), adsorbent dosage effect and concentration effect of the adsorbates were studied.

### [6] *Preparation of simulated wastewater (stock solution)*

All the experimental containers were properly washed and rinsed with distilled water. The stock solutions were prepared by measuring out 1000ml of distilled water. One gram (1g) of the Cadmium (II) was added to the Container containing 1000ml of distilled water. Proper mixture was ensured. A stock solution of 1000mg/L of Cadmium was prepared.

[7] **Treatment of the Wastewater with the Adsorbent**

250ml of the stock solution was drawn and poured into 250ml Erlenmeyer flask. 3g of the adsorbent was measured out using Electronic weighing balance. It was added into the 250 ml of the stock sample and was thoroughly shaken together for proper mixing. 20 ml each of this mixture (adsorbent and adsorbate) were immediately drawn and poured into eleven different 100-ml Erlenmeyer flasks. The first 20 ml sample was immediately filtered at zero minute into a sample container using Whatman filter paper. The other 20 ml samples were placed on different magnetic stirrers and were stirred at different time between 1 and 100 minutes using standard methods recommended for examination of water and waste water [25]. The stirring was to make adsorption more effective. The heavy metal ion concentration (Cd) of the treated wastewater was analyzed at the time interval of 10 minutes, between 0 and 100 minutes.

Subsequent adsorption experiments were carried out by using optimized parameters. Using 20ml of the stock solution at 50-70 minutes depending on the particular modified melon husk used. The dosages of the adsorbents were varied between 0.2 g to 1.0 at 0.2 g interval, while the time and adsorbate concentration were kept constant.

Considering the effect of adsorbate concentration, the concentrations of the adsorbate were varied using distilled water at constant time and adsorbent dosage. Concentration of adsorbed metal ions (Cd(II)) at any of these experiments were determined spectrophotometrically by using standard method of [23].

The concentrations of the stock solutions were determined to serve as control sample or initial concentrations. Residual metal ion concentrations in the filtrate (after adsorption) were measured by atomic adsorption spectrophotometry (AAS) model 9100 x Philips, England). The amount of cadmium(II) adsorbed qt, (mg/l) at time (t) were calculated by using the following equation:

$$q_{t(\text{mg/L})} = \frac{(C_0 - C_e) V}{m}$$

Where  $C_0$  and  $C_e$  are the metal ion concentration in mg/L initially and at given time, t respectively, V, is the volume of the adsorbate and M, the mass of the adsorbent in gram.

While  $q_{t(\text{mg/g})} = \frac{(C_0 - C_e) X (V/1000)}{m}$

The percentage of the metal ion removed ( $R_{\text{metal}} \%$ ) from solution was calculated by using the following

equation.

$$R_{\text{Cd(II)}} (\%) = \frac{C_0 - C_e}{C_0} \times 100$$

$$R_{\text{Pb(IV)}} (\%) = \frac{C_0 - C_e}{C_0} \times 100$$

$$q_e = C_0 - C_e$$

[8] **Sorption Isotherms**

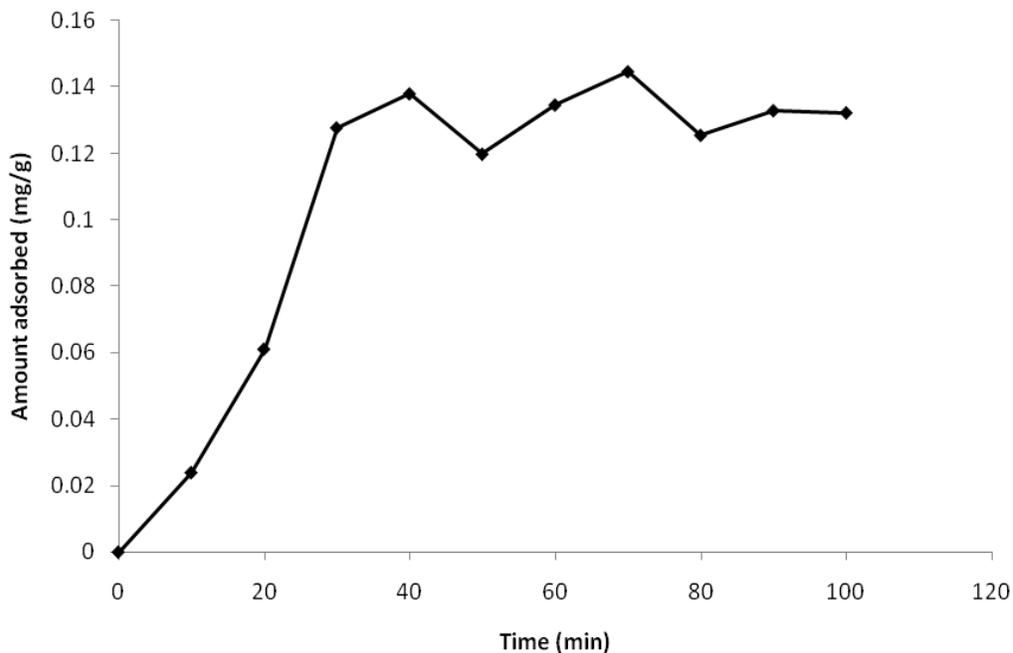
Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Equilibrium studies that give the capacity of the adsorbent and equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Langmuir and Freundlich isotherms are the earliest and simplest known relationships describing the adsorption equation [24,25]. These two isotherm models were used to assess the different isotherms and their ability to correlate experimental data.

[9] **Sorption Kinetics**

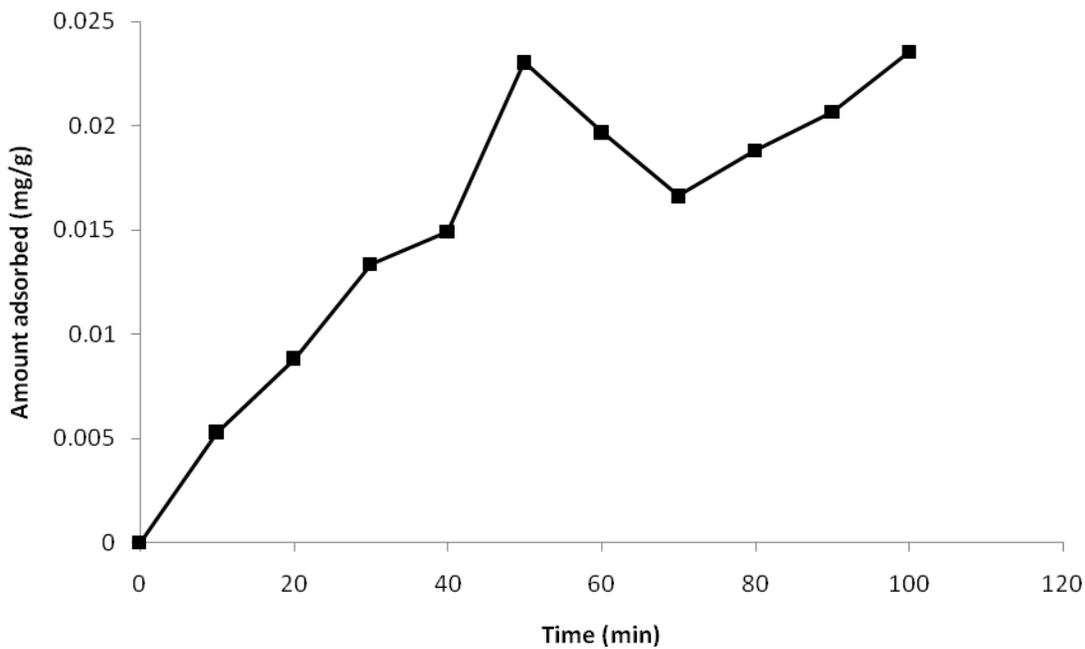
The rate of adsorption of a molecule unto a surface is an essential parameter when designing batch sorption systems, consequently it is essential to establish the time dependence of such systems under various process conditions. In an attempt to describe the sorption rate and confirm the reaction mechanism of  $\text{Cd}^{2+}$  onto melon husk, two kinetic models were applied to the experimental data. The first model was based on the assumption that sorption of metal ions onto the melon husk was reversible and followed a first order rate kinetics [26]. The experimental data were further evaluated based on the pseudo-second order kinetic rate model proposed by [27].

**RESULT AND DISCUSSION**

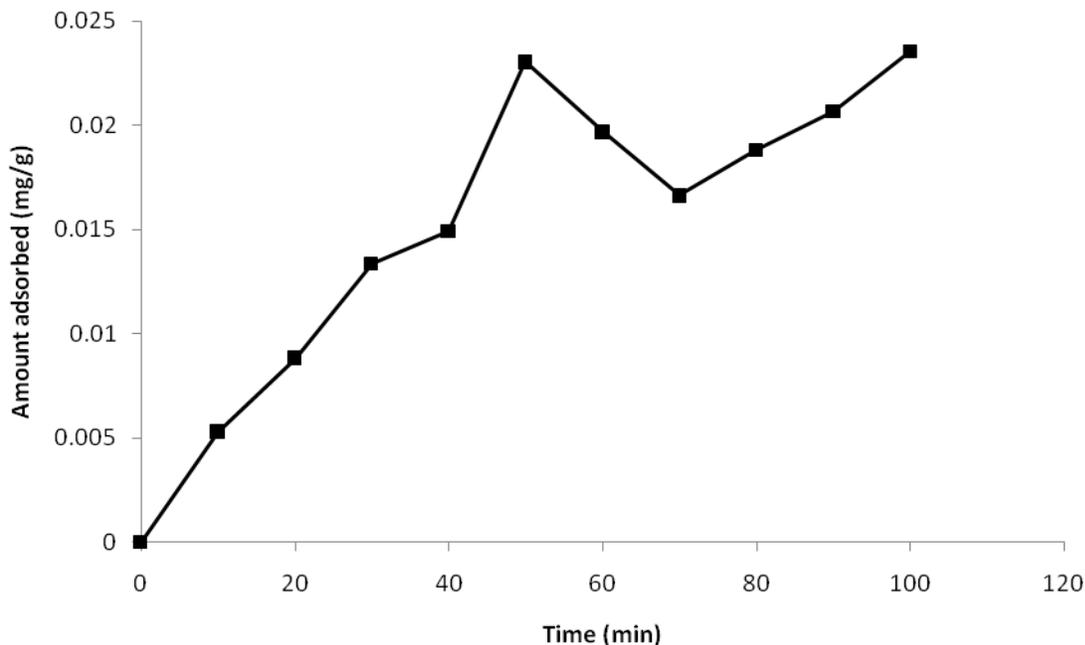
The results of the effects of contact time on cadmium Sorption by the adsorbents is presented in Figures 1 and 2. There was rapid adsorption of Cd(II) by  $\text{H}_2\text{SO}_4$  modified melon husks for the first 40 minutes. Increase contact time increased percentage removal of cadmium until equilibrium adsorption was established within 70 min with 90.07%(1.7352 mg/L) adsorption. Sorption by NaOH modified melon husk adsorbent showed that the sorption of cadmium increased with time though the rate of increase was small with equilibrium attained within 50 minutes.



**Fig. 1 :** Effect of contact time on adsorption of  $Cd^{2+}$  ;  $H_2SO_4$  (Volume 250 mL, adsorbent dose 3 g)



**Fig. 2 :** Effect of contact time on adsorption of  $Cd^{2+}$  ;  $NaOH$  (Volume 250 mL, adsorbent dose 3 g)



The results of the effects of the adsorbent dosage on Cd(II) sorption is presented in Figure 3 and 4 and shows that cadmium adsorption is adsorbent dosage dependant. The percentage removal of cadmium increased with increasing adsorbent dosage up to a dosage of 0.6 g of the adsorbent (H<sub>2</sub>SO<sub>4</sub> modified

melon husk), at which point the maximum adsorption was attained. After this, any other additional dose did not have any effect, the sorption decreased. The adsorption of cadmium by NaOH modified melon husk increased in a linear form with the highest dose achieving the highest adsorption.

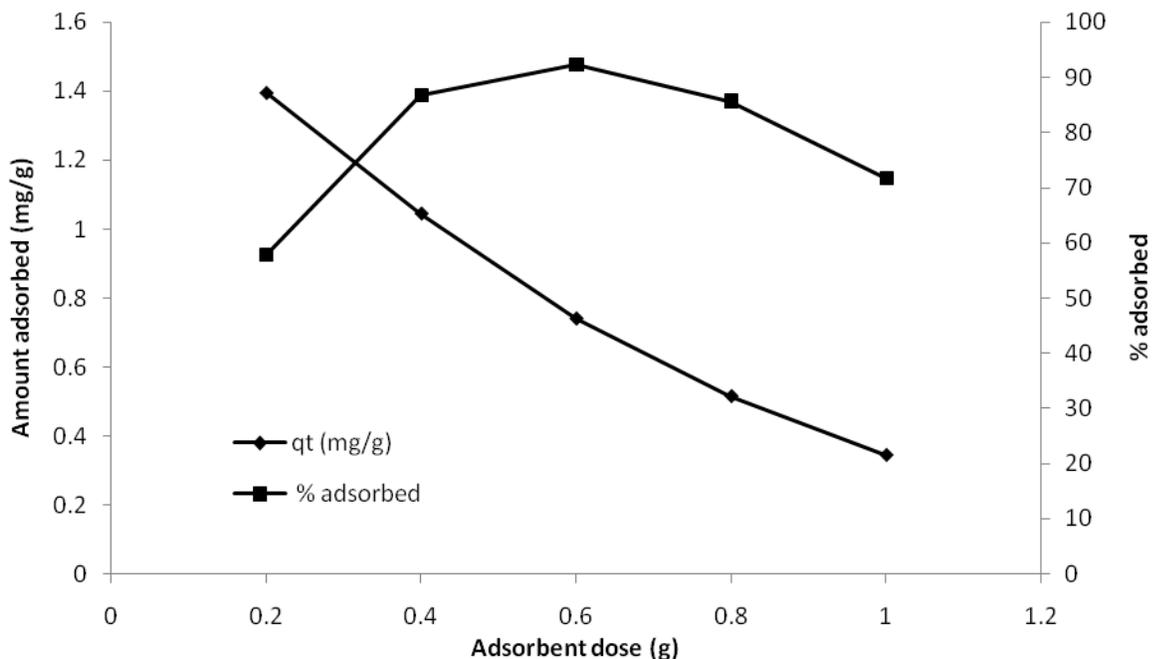
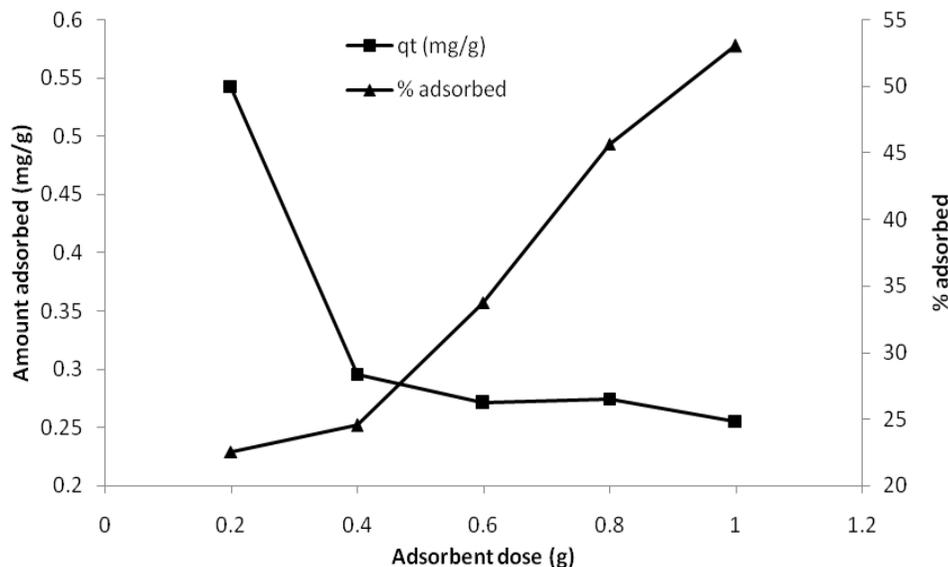


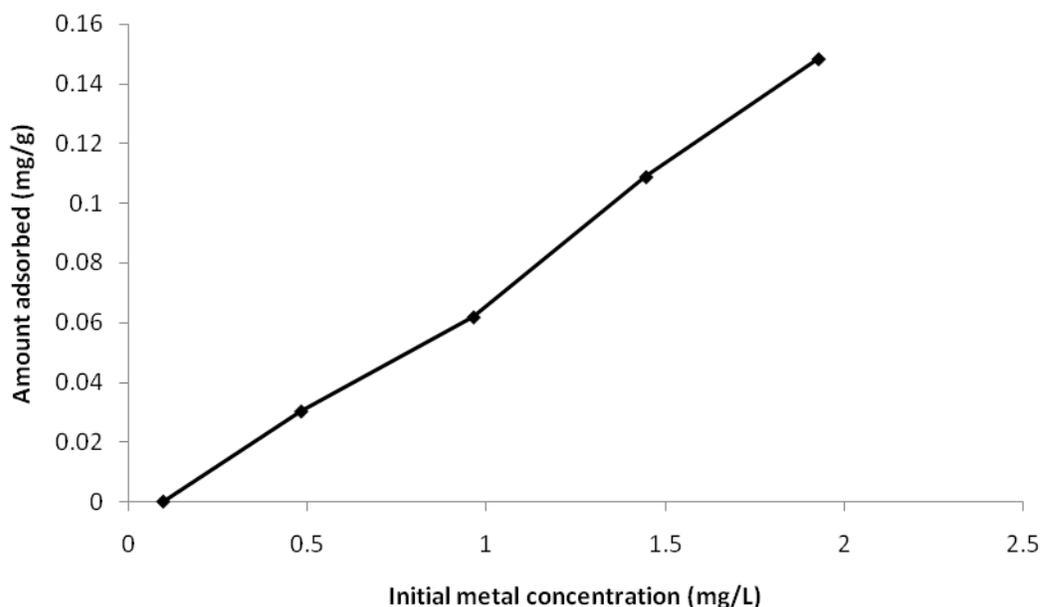
Fig. 3 : Effect of adsorbent dose on adsorption of Cd<sup>2+</sup>; H<sub>2</sub>SO<sub>4</sub> (Volume 250 mL)



**Fig. 4 :** Effect of adsorbent dose on adsorption of  $Cd^{2+}$  ; NaOH (Volume 250 mL)

The adsorption of cadmium by  $H_2SO_4$  modified melon husk did not show strict dependency on the concentration of the adsorbate, (Fig 5). This was attributed to the high efficiency of  $H_2SO_4$  modified melon husk in removing cadmium. This high efficiency of  $H_2SO_4$  activated melon husk has been

shown throughout this study. The adsorption of cadmium by NaOH modified melon husk showed high dependency on adsorbate concentration. Decrease in concentration resulted in increase in adsorption, though there was a drop at the least adsorbate concentration.



**Fig. 5 :** Effect of initial metal concentration on adsorption of  $Cd^{2+}$  ;  $H_2SO_4$  (Adsorbent Dose 3 g, Volume 250 mL)

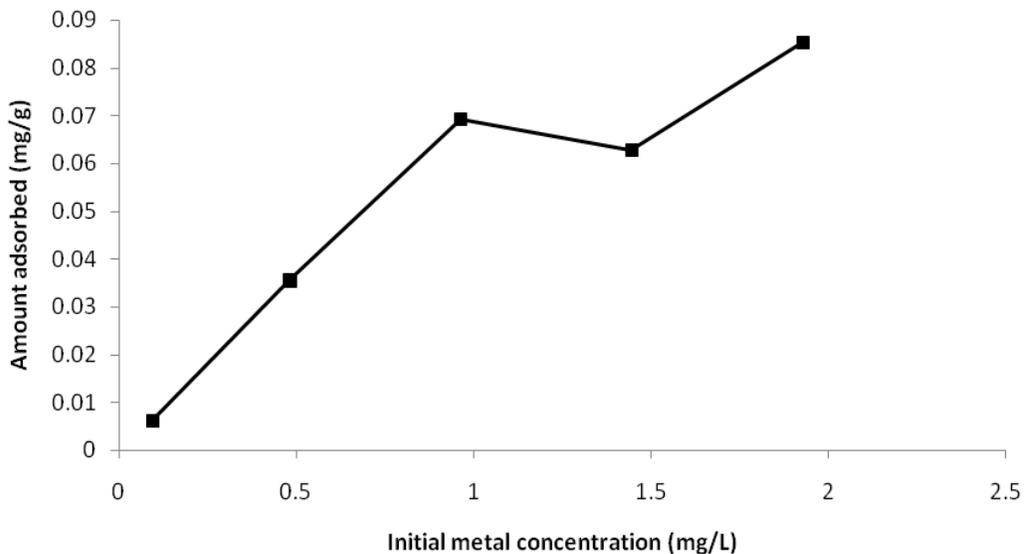


Fig. 6 : Effect of initial metal concentration on adsorption of  $\text{Cd}^{2+}$  ; NaOH (Adsorbent Dose 3 g, Volume 250 mL)

Adsorption isotherm model for sorption of cadmium and lead is presented in fig 7 and 8 respectively.

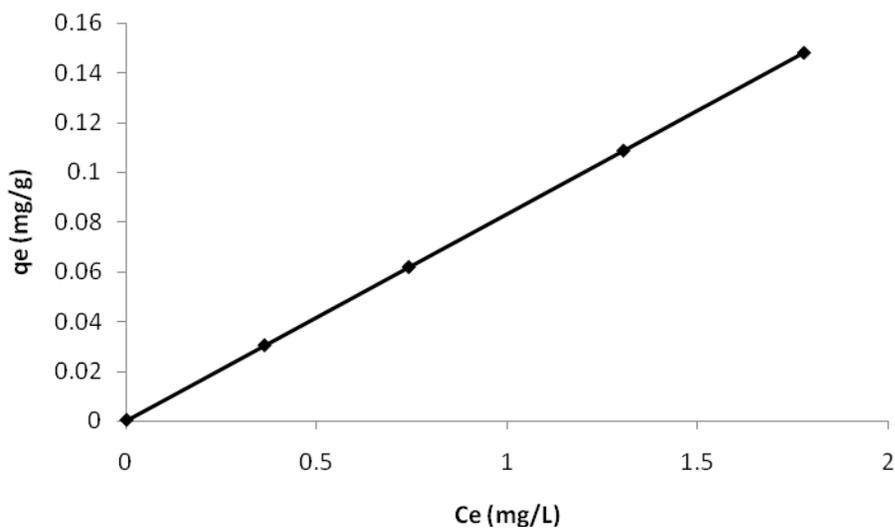
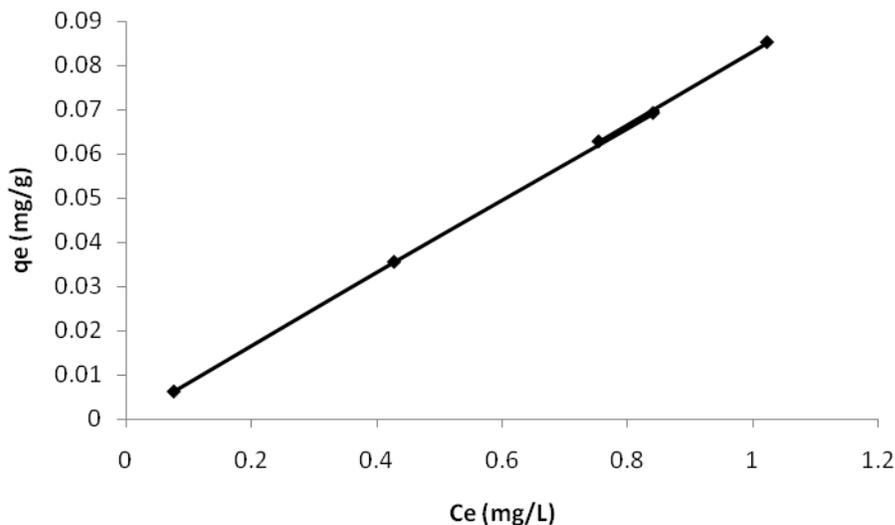


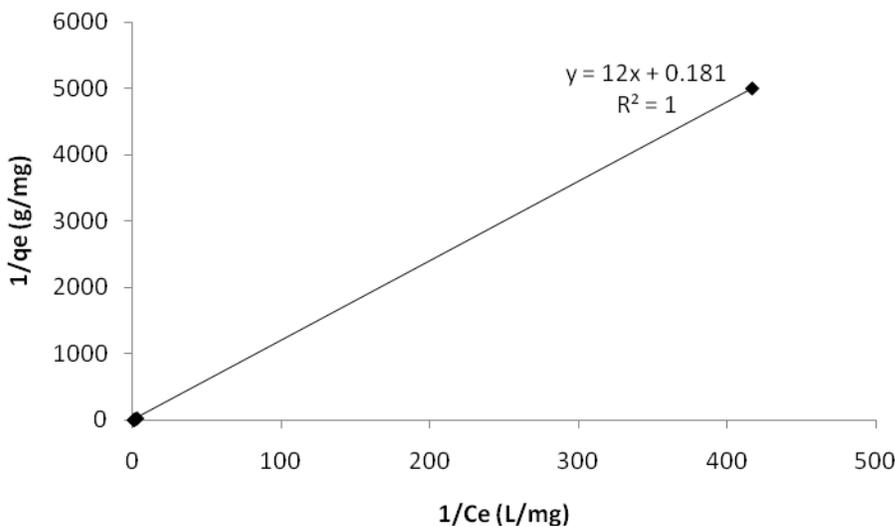
Fig. 7 : Adsorption isotherm model for sorption of  $\text{Cd}^{2+}$  ( $\text{H}_2\text{SO}_4$ )



**Fig. 8 :** Adsorption isotherm model for sorption of Cd<sup>2+</sup> (NaOH)

A plot of  $q_e$  against  $C_e$  (Fig. 7 and 8) yielded straight lines and indicates a good fit of the isotherm to the experimental data. The linear plots of  $1/q_e$  against  $1/C_e$  show that adsorption followed the Langmuir model (Fig. 9 and 10). The correlation coefficient  $R^2$

is 1 for sorption of cadmium by both modified melon husks. The plots of  $\text{Log } q_e$  against  $\text{Log } C_e$  show that adsorption also followed the Freundlich model (fig.11 and 12). The correlation coefficient  $R^2$  is also 1 for sorption of Cd(II) by both



**Fig. 9:** Langmuir equilibrium isotherm model for sorption of Cd<sup>2+</sup> (H<sub>2</sub>SO<sub>4</sub>)

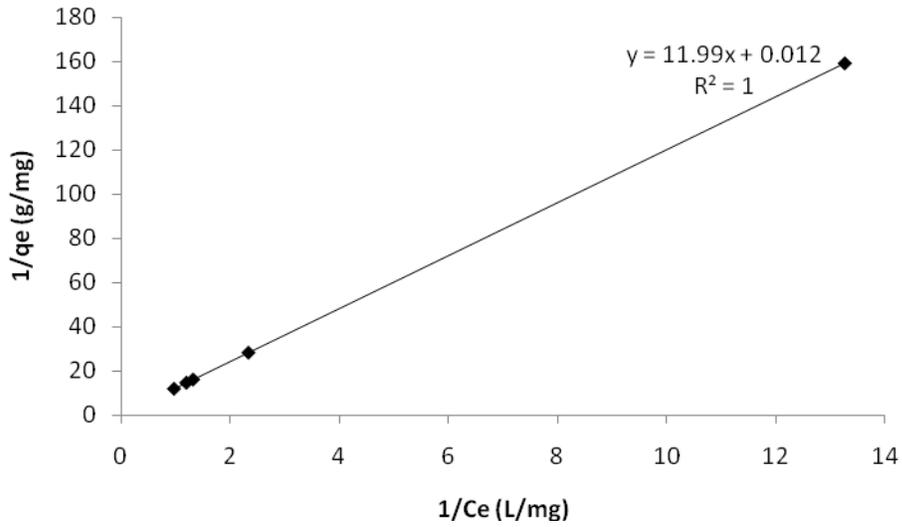


Fig. 10 : Langmuir equilibrium isotherm model for sorption of  $Cd^{2+}$  (NaOH)

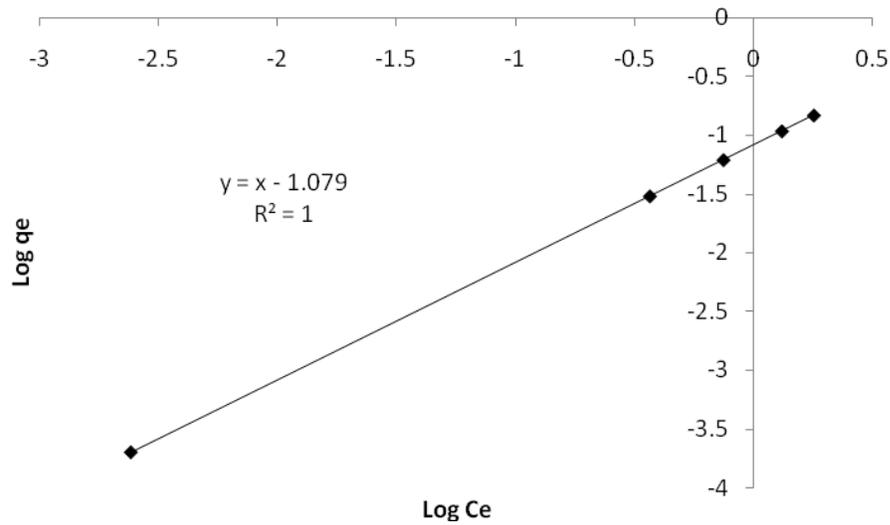


Fig. 11 : Freundlich equilibrium isotherm model for sorption of  $Cd^{2+}$  ( $H_2SO_4$ )

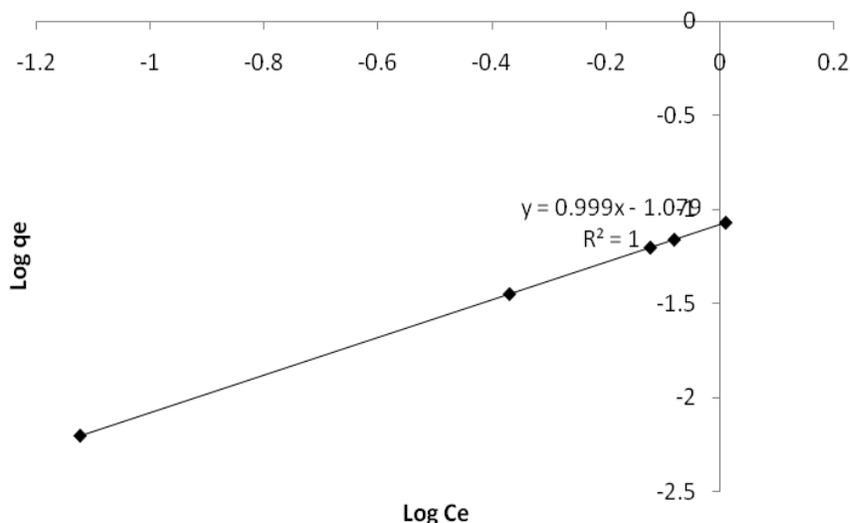


Fig. 12 : Freundlich equilibrium isotherm model for sorption of Cd<sup>2+</sup> (NaOH)

The rate of adsorptions of Cd(II) onto H<sub>2</sub>SO<sub>4</sub> and NaOH modified melon husks were fitted into pseudo-second order adsorption kinetics. The data showed that, modified melon husk enhanced the equilibrium sorption capacity of the melon husks towards the metal ion. The *r*<sup>2</sup> values (coefficient of determination) are 0.7979 and 0.8486 (Fig.13 and 14).

The result of the experiments showed that modified melon husk has the potential of removing cadmium from waste water-like many other agricultural waste products. [28] in their review showed that agricultural waste products like sugarcane bagasse, rice husk, coconut husk, oil palm shell, neem bark e.t.c have a great potential for the elimination of heavy metals from waste water.

Results obtained from the analysis of filtrates while varying the contact time of the adsorbent with the adsorbate showed that the removal of cadmium from waste water increased with increasing contact time. According to [29], the results obtained from varying the contact time of the adsorbent with the adsorbate showed that the removal of chromium and lead from drill cutting extract increased with increasing contact time and attained equilibrium at 90 and 120 min for both activated palm kernel shell (APKS) and activated palm kernel husk (APKH), respectively.

For the adsorption of cadmium in the present work, equilibrium was attained at 70 min for H<sub>2</sub>SO<sub>4</sub> modified melon husk. But for the adsorption by NaOH modified melon husk, the sorption of cadmium increased with time though the rate of increase was small. The result of the adsorption of cadmium by *Platanus orientalis* leaf (POL) indicates

that cadmium adsorption increased with increasing time and became almost constant after 60 min for POL and 60 min for its ash [30]. Similar results showed that adsorption of cadmium increase with increased in contact time and became almost constant after 45 min for rice husk and 30 min for its ash [31]. [32,33] reported that adsorption of Cd(II) is dependent on contact time. These findings are in agreement with the result of the present work.

The amount of adsorbent employed was found to influence the efficiency of the adsorption process of cadmium. The percentage removal of cadmium increased with increasing carbon and maximum sorption was attained at 0.6 g for H<sub>2</sub>SO<sub>4</sub>. While maximum adsorption was attained at the highest dose by NaOH modified melon husk. Once the maximum adsorption sets in, even with further increase in the dose of adsorbent there was no further adsorption. This was in agreement with [34] who reported that adsorption of Cd(II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution.

According to [29] the percentage removal of lead and chromium increases with increased carbon dosage. The performance of the adsorbent was evaluated by [35] for the removal of lead. The dose of the adsorbent was varied between 1.0 and 3.0g/100ml. Percentage lead removal increased significantly as the amount of adsorbent added increased. Adsorbent dosage of 2.0g/100ml was required to remove 99% of lead in aqueous solution. This showed that as the dose of adsorbent increased, there was increase in the available exchangeable sites for lead. [36] confirmed that Cd(II) and Pb(II) removal were dependent on adsorbent dosage.

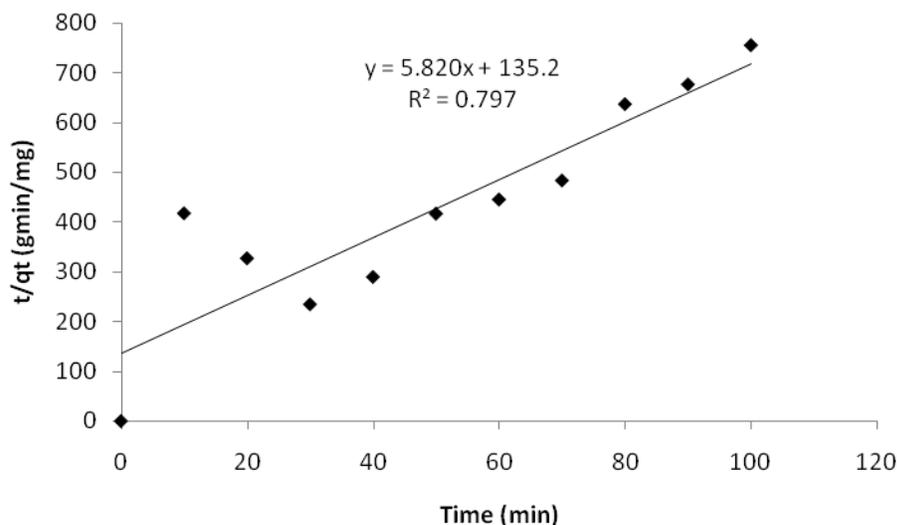


Fig. 13 : Pseudo-second order sorption kinetics of  $Cd^{2+}$  ( $H_2SO_4$ )

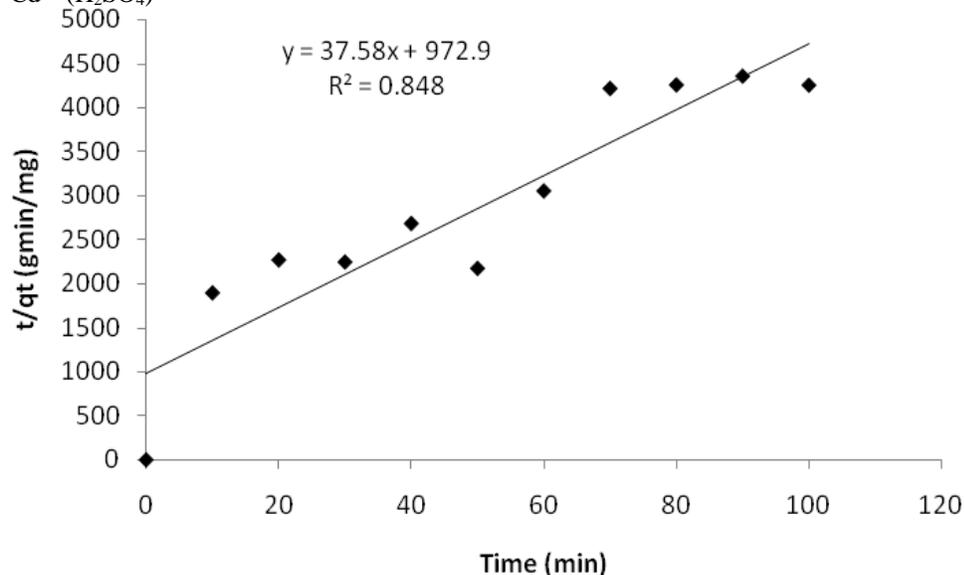


Fig. 14 : Pseudo-second order sorption kinetics of  $Cd^{2+}$  ( $NaOH$ )

The percentage removal of cadmium by the adsorbents increased with decreasing adsorbate concentration. At lower concentration, cadmium ion in the solution interacted with the binding sites and higher percentage adsorption was facilitated. At higher concentration, more cadmium ions were left unabsorbed in solution due to the saturation of the binding site. [37] reported that sorption efficiency of Copper decreased with increase in adsorbate concentration.

[32] reports that adsorption of Cd(II) on phosphate treated rice is dependent on adsorbate concentration.

The studies of [38] on the removal of Chromium (VI) from aqueous waste showed that the removal was generally most effective at low concentration. The percentage removal of Cd(II) from the least  $C_0$  (initial concentration) was 78.2% for NaOH modified melon husk while that of  $H_2SO_4$  did not show much dependency on the concentration. This difference in rate of adsorption is because adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cations [39]. [39] agreed with this from the results of their work on removal of Cadmium from

wastewater using tea waste. [40] in another study to find out the effect of metal type on adsorption concluded that the adsorption efficiency is also dependent upon the type of metal. Not more than 76% removal of Ni ions achieved with the same conditions that gave rise to 94 and 60 % removal of Pb and Cd respectively.

[41] studied the percentage removal of Cd, Pb and Phenol at the same conditions. Pb was found to attain above 99 % removal both at minimal and optimal conditions. For Cd it was 26 and 94.5 % respectively. Phenol was 51% for minimal and 76% for optimal conditions. These results agreed with the current work.

The equilibrium sorption data were represented by Langmuir and Freundlich isotherm models. According to [42], in the equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize. The data fitted to Langmuir, Freundlich and Dubinin-Radushkevich isotherm. The linearized plot of both Langmuir and Freundlich produced  $R^2$  values are 1 for both. This shows that  $H_2SO_4$  and NaOH modified melon husk are efficient adsorbents in the removal of Cd.

Isotherm studies for heavy metal adsorption on rice husk by [43] showed that adsorption data fitted better with Freundlich than Langmuir model. Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions fitted to Freundlich type isotherm model. While Langmuir model fitted better in the biosorption of lead from industrial wastewater using *Chrysophyllum albidum* seed shell, [35]. [37] and [44], in their separate work on heavy metal adsorption using various agricultural wastes reported that the data fitted better to Langmuir isotherm model.

The positive linear plots of the sorption kinetics of both modified melon husk showed that the experimental data were fitted into pseudo-second order sorption kinetics. [27] in the sorption kinetics of  $Pb^{2+}$  and  $Cu^{2+}$  ions, reported that the experimental data were fitted into pseudo- second order kinetics. The coefficient of determination,  $r^2$ , from the pseudo-second order rate model showed that,  $r^2$  values are greater than 0.990 for both metals with or without modification. The  $r^2$  values of the pseudo-second order rate for the present work are 0.7979 and 0.8486 which is similar to that obtained by [27]. [45] reported that the experimental data of the adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, followed pseudo-second order adsorption kinetics. [44] also reported a similar result of pseudo-second order sorption kinetics on the biosorption of cadmium ions from aqueous solution using pomelo peel, an

agricultural waste. The coefficient of determination values indicates that the modified melon husk is an excellent biomaterial for the removal of metal ion from industrial waste water.

The  $r^2$  values for the pseudo-second order kinetics showed that NaOH modified melon husk was a better adsorbent than  $H_2SO_4$ .

## CONCLUSION

Based on the findings of this research, the study concludes that melon husk activated with sulphuric acid and sodium hydroxide can be used effectively in the remediation of industrial waste water. The study also recommends that industries reduce their use of these heavy metals or better still find alternative material to it, since it is known that even though metals are adsorbed, they can still find their way into the environment.

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