

RESEARCH ARTICLE

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Evaluation of the adsorptive capacity of Activated *Egusi* Peels (AEP) for the removal of heavy metals from aqueous solutionsI. H. OWAMAH^{1*}, J. O. OJEDIRAN² AND T. A. ADEKANYE³^{1*}Civil Engineering Department, Landmark University, P.M.B.1001, Omu-Aran, Kwara State, Nigeria^{2&3}Agricultural and Biosystems Engineering, Landmark University, Omu-Aran, Kwara State, Nigeria**Abstract**

The removal of Pb (II) and Cu (II) by adsorption onto activated melon peels (AEP) adsorbent was investigated in this present paper. The adsorption data was well described by both the Langmuir and the Freundlich isotherm models. Adsorption was found to increase with increase in temperature, contact time and adsorbent dose but decreased with increase in pH. Pseudo-first order kinetic model was found suitable for describing the kinetics of the adsorption process. The Freundlich isotherm model k_f was 3.43 for Pb (II) and 4.05 for Cu (II) signifying a preferential sorption for Cu (II) onto AEP in any industrial wastewater containing the two heavy metals. The Freundlich parameter n being less than unity indicates that the adsorption of Pb (II) and Cu (II) onto AEP was by physical sorption. Results from this study show that AEP could be used economically, for removing heavy metals from wastewater.

Keywords: Activated Egusi Peels (AEP), heavy metal adsorption, kinetic and isotherm study.

1. Introduction

Urbanization and industrialization have led to an increase in the amount of heavy metals in the environment. These heavy metals have been of great concern to both environmental scientists and environmental engineers, as a result of their negative effects on the environment; especially the receiving streams [1]. These heavy metals are toxic even at low concentrations. They are also non biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms which could lead to series of health problems to man.

The increased use of lead and copper for batteries and other applications, such as pigments, polyvinyl chloride stabilizers and plating, has led to a sharp global increase in the amount of lead and copper found in the environment [2]. Wood pulp production, paperboard mills and metal cleaning processes generate metal ions that are very toxic. It is therefore very necessary to treat such wastewater, before final disposal into the water bodies [2].

Lots of conventional methods like chemical precipitation, electro dialysis, reverse osmosis, adsorption by commercial activated carbon e.t.c. are used for removing heavy metals from wastewater but these technologies are quite expensive and not easily affordable by industries in developing nations. Again, industrial wastewater in many developing countries

undergoes little or no treatment before final discharge into receiving streams [3]. This could be attributed to the cost of treatment using high-tech methods and/or the non-availability of such technologies within the reach of the striving to survive industries. A lot of researchers have studied the use of low cost organic materials as substitutes for commercial activated carbon. Some of these studies are; adsorption of heavy metals from polluted water using activated carbon from date-pits [4], ferrihydrite and leaf compost for wastewater treatment [5], kinetic and equilibrium modeling of nickel adsorption by modified cassava peels [6], [7] has reported on the potential use of rice straw as an adsorbent for removal of mercury ions at optimum pH range of 4-7.

Egusi (*C. Lanatus*) is a wild melon of the gourd family that looks in appearance like a water melon. Though the flesh is not eatable, the seeds are a valuable source of food in Africa. The seeds contain nearly 50% edible oil and another 30% pure protein. *Egusi* seeds are used for preparing various kinds of food but majorly for cooking *Egusi* soup in West Africa, after peeling and grounding. These many uses of *Egusi* ,has led to the generation of large amount of *Egusi* peels, which is normally burnt in the open or used as fire starters in rural kitchens of developing countries. This disposal method is wasteful and impacts negatively on the climate.

This study therefore explored the possibility of using activated *egusi* peels for the adsorption of lead

and copper ions from wastewater. The adsorption kinetics and isotherms were also evaluated. The study also investigated the effect of varying temperature, pH and adsorbent dose on adsorption of lead and copper from aqueous solutions, using activated *egusi* peels in order to determine the optimum conditions for the design for large scale adsorption columns that will utilize AEP for heavy metals removal. Results from this study will be useful in assessing the suitability of lead and copper ion removal from wastewater using AEP.

2. Materials and Method

2.1 Collection and preparation of the adsorbent

Egusi peels were collected from the waste bin of a middle class family in Ibusa, Oshimili North Local Government Area of Nigeria. These *egusi* peels were washed with deionized water and allowed to air-dry. This was followed by sun-drying for five days. The dried samples were ground using mechanical grinder and then sieved through a B.S. standard screen to obtain a particle size of 100 μ m and stored in a plastic container for further analysis.

2.2 Activation and purification of the biomass

It is often necessary to activate a solid before using it as an adsorbent for sorption studies. The purpose of activation is to increase the surface area of the solid by introducing a suitable degree of porosity into the solid matrix [8]. Again, activation may also produce structural defects in solids, which may be favorable to sorption processes [9]. The experiments on activation and purification of the biomasses were carried out according to the previous works of [9]. 500 g of finely divided biomass was activated and at the same time purified by soaking in excess 0.3 M HNO₃ for 24 hours to remove any metals and debris that might be in the biomass prior to experimental metal ion exposure. This was followed by washing thoroughly with deionized water until a pH of 7 \pm 0.1 was attained and then air-dried. The air dried biomass was then washed with deionized water and re-suspended in 1.0M hydroxylamine to remove all O-acetyl groups. To remove all other soluble materials, the biomass was washed with deionized water.

2.4 Procedure for sorption and analysis

12 g of sorbent dose in metal solution were used for the experiment. 1000g stock solutions were prepared using copper nitrate and lead nitrate which were diluted with distilled water to prepare working solutions. Apart from the effect of pH and temperature experiments, all other experiments were carried out in the pH range of 2-2.2 and room temperature (27 \pm 3⁰C). Agitation of the mixture was done by a rotary shaker at 160 rpm. The sample was allowed to settle for about 60 seconds following the end of the experiment. Thereafter the supernatant sample was analyzed for its Pb (II) and Cu (II) concentration, through the use of atomic absorption spectrophotometer. Isotherm sorption studies were carried out at adsorbent dose of 2g/l-12g/l while keeping the initial Pb (II) and Cu (II) concentrations constant at 5..20mg/l for Pb (II) and 4.20 mg/l for Cu (II) for the various experiments.

3. Existing Theory

3.1 Calculation of the degree of metal ion removal

The amount of Pb(II) and Cu(II) removed by the biomass during the series of batch investigations were determined using a mass balance equation expressed as shown in Equation (1);

$$q = \frac{V}{M}(C_0 - C) \quad (1)$$

where;

q = Fractional coverage of the surface (mg/g)

C = Metal-concentration concentration (mg/l) at time t

C₀ = Initial metal-ion concentration in solution (mg/l)

V= Volume of solution (L)

M= Mass of obvious used (g)

3.2 Calculation of metal ion removal efficiency

The amount of sorbed Pb (II) and Cu (II) was expressed as sorption percent, %S [8]

$$\%S = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

Where C₀ and C are as defined in Eq. (1)

3.3 Equilibrium isotherm

Sorption equilibrium isotherms provide fundamental physico-chemical information for evaluating the applicability of a sorption process as a

unit operation usually described by isotherm models whose parameters express the surface properties and affinity of the adsorbent. Two adsorption isotherm models were used to fit the experimental data. The Langmuir and the Freundlich isotherm models were carefully applied to study the adsorption of Pb (II) and Cu (II) onto the activated melon peels biomass.

3.3.1 The Langmuir Isotherm

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The Langmuir isotherm is expressed as shown in Equation (3)

$$q = \frac{q_m K_l C}{1 + K_l C} \quad (3)$$

Where K_l =Langmuir isotherm constant ($l g^{-1}$), q_m = Langmuir monolayer adsorption capacity ($mg g^{-1}$). Solving Equation(3), gives Equation(4):

$$\frac{C}{q} = \frac{C}{q_m} + \frac{1}{K_l q_m} \quad (4)$$

The experimental data were fit into Equation (4) by plotting C/q against C .

3.3.2 Favourability of Adsorption of Pb (II) and Cu (II) onto AEP

The essential characteristics of the Langmuir isotherm can be described by a separation factor R_L , which is defined by [10], as shown in Equation (5)

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 = initial concentration of heavy metal ion (mg/l) and K_L is the Langmuir constant, which indicates nature of adsorption. The separation factor R_L indicates the isotherm shape and tells whether the adsorption process is favourable or not.

3.3.3 Freundlich Isotherm Model

Freundlich model was also chosen to estimate the adsorption intensity of the adsorbate towards the adsorbent (biomass) and is represented by Equation (6) [10].

$$q = K_f C^n \quad (6)$$

where q = fractional coverage of the surface (mg/mg), C = the amount of metal ion concentration at time t in (mg/l); K_f and n are the Freundlich constants.

Taking the natural logarithm of both sides of Equation (6), we have

$$\ln q = \ln K_f + \frac{1}{n} \ln C \quad (7)$$

A plot of $\ln q$ against $\ln C$ that yields a straight line indicates the confirmation of the Freundlich adsorption isotherm model. The constants $1/n$ and $\ln K_f$ can be determined from the slope and intercept of plot [11].

3.4 Kinetics of sorption

The kinetics of sorption is one of the most important factors for predicting the rate at which sorption takes place for a given system and also it is very essential in understanding adsorption system design with a given adsorption residence time and reactor mechanism. However, sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the adsorbent material which also influences the sorption process and mechanism [12]. The linear form of pseudo first order kinetic model can be expressed as shown in Eq. (8):

$$\ln(q_m - q) = \ln q_m - K_1 t \quad (8)$$

where q_m = maximum adsorption capacity and is equal to q_e (adsorption capacity at equilibrium) in mg/g , q is the adsorption capacity(mg/g) at any time t (h), K_1 is the pseudo first order rate constant(h^{-1})

4. Results and Discussion

4.1 Effect of varying pH

As shown in **Figure 1**, the percentage amount of lead and copper ions adsorbed decreased with increase in pH. This suggests that the adsorption of Pb (II) and Cu (II) from wastewater using activated melon peels as bio-sorbent is better in acidic medium.

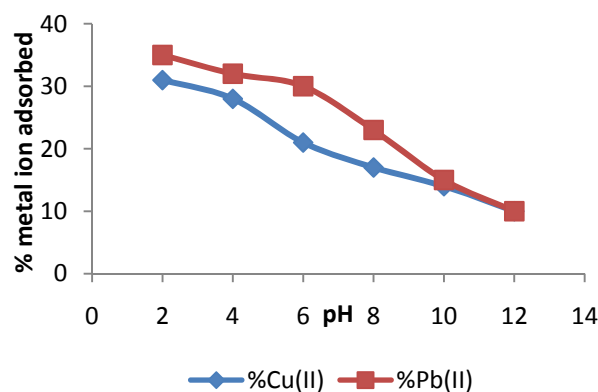


Figure 1: Effect of pH on Pb (II) and Cu (II) adsorption

4.2 Effect of adsorbent dosage

The effect of adsorbent dosage on adsorption of Cu (II) and Pb (II) ions was studied at constant initial

metal ion concentration of 5.20 mg/l for Pb (II) and 4.20 mg/l for Cu(II) at constant pH of 2 and constant agitation time of 20 minutes. 2, 4, 6, 8, 10 and 12g of the adsorbent were weighed into five well labeled flasks for the experiment as has been done in [8]. **Figure 2** shows that the adsorption of Pb (II) and Cu (II) increased with increase in dosage.

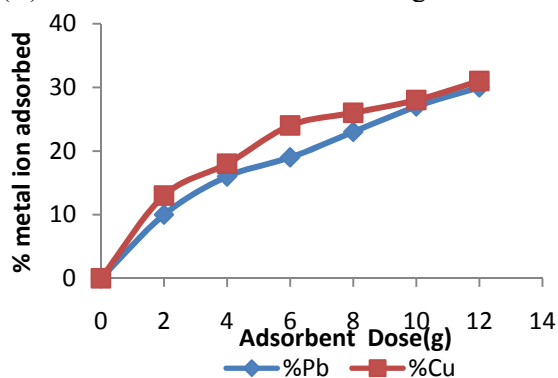


Figure 2. Effect of adsorbent dose on adsorption

4.3 Effect of contact time on adsorption

The effect of contact time on Cu (II) and Pb (II) ions removal by the activated *egusi* peels adsorbent was studied at constant initial metal ion concentration of 5.20mg/l for Pb (II) and 4.20 mg/l for Cu (II) at different contact times of 20, 40, 60, 80, 100 and 120 minutes. The result of the effect of contact time on adsorption as shown in **Figure 3** reveals that adsorption of Cu (II) and Pb (II) onto the activated *egusi* peels adsorbent increased with increase in contact time and was rapid.

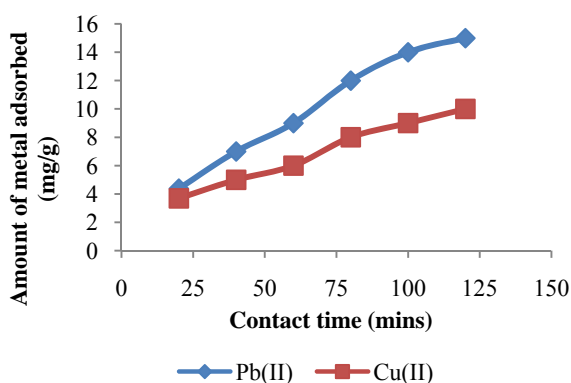


Figure 3: Effect of contact time on adsorption

4.4 The Effect of temperature

The effect of temperature on adsorption of Cu (II) and Pb (II) ions was studied by conducting

different sets of experiments at initial metal ion concentration of 5.20 mg/l and 4.20mg/l for Cu (II) at different temperature i.e. 15, 25, 35 and 45°C and at different contact time (20, 40, 60, 80 and 120 minutes) for each of the chosen temperature. Results obtained as shown in **Figure 4** and **Figure 5**, show that adsorption of Pb (II) and Cu (II) increased with increase in temperature. This increase in adsorption capacity of AEP with increase in temperature indicates an endothermic process. This increase could be as a result of increases in the number of active surface sites for adsorption by AEP at higher temperature [13].

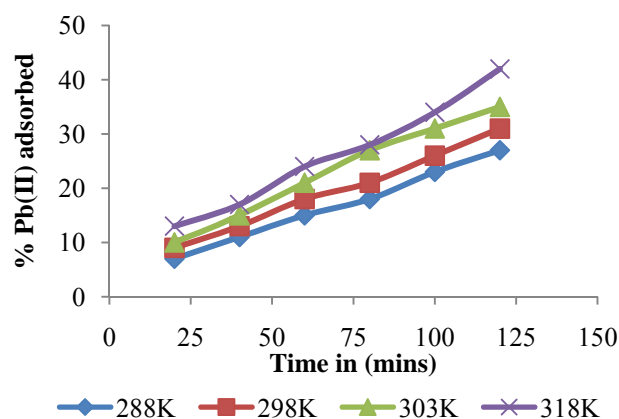


Figure 4 : Effect of temperature on Pb (II)

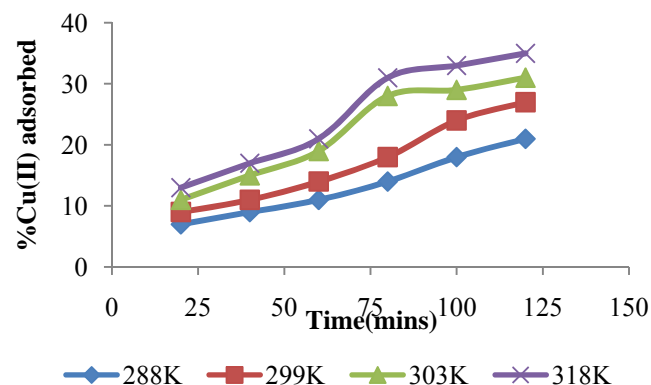


Figure 5 : Effect of temperature on Cu (II)

4.5. Adsorption isotherms

The adsorption of Cu (II) and Pb (II) ions onto AEP was studied using the Langmuir and Freundlich isotherms with the quality of fit being assessed through the correlation coefficient value. From the Langmuir plots of **Figure 6** and **Figure 7**, q_m , which is a mass measure of maximum adsorption capacity corresponding to complete monolayer coverage was obtained as 0.83 mg/g and 0.75 mg/g for Pb (II) and Cu (II) respectively. It therefore means that AEP has a

higher adsorption capacity for Pb (II) than Cu (II). Though these q_m values are relatively low in comparison with the adsorption capacity reported for other bio-sorbents in literature [14], *egusi* peels are highly inexpensive and they are found in high quantity in the West African environment. With this, AEP could be more economical in the removal of metal ions from industrial wastewater. Computed R_L values are shown in Table 1 for Pb (II) and Cu (II) ions. R_L values lie between 0 and 1 for Cu (II) and Pb (II). This indicates that the adsorption of Pb (II) and Cu (II) onto AEP is favourable. R_L for Pb (II) =0.38 and that of Cu (II) =0.32. Because the R_L value of Cu (II) is less than that of Pb (II), it shows that Pb (II) will be adsorbed at a faster rate than Pb (II) from industrial wastewater. The observed favorable values of R_L also suggests that high concentrations of Cu(II) and Pb(II) ions in an effluent will not be a limiting factor in the ability of AEP to adsorb the metal ions.

From the Freundlich plots of Figure 8 and Figure 9, the Freundlich isotherm model is also an appropriate model for the sorption study of Cu (II) and Pb (II) ions onto AEP. The Freundlich isotherm constants K_f and n are determined from the intercept and slope of Figure 8 and Figure 9 for Pb (II) and Cu (II) respectively. The determined Freundlich isotherm parameters are shown in Table 2. The K_f value of Cu (II) which is 4.05 is greater than that of Pb (II) which is 3.43 indicating that Cu (II) has greater adsorption tendency towards AEP, than Pb (II). The Freundlich model parameter (n), which is a measure of adsorption intensity, is 0.37 for Pb (II) and 0.29 for Cu (II) indicating a preferential sorption for Cu (II) by AEP. In this study, n values are less than unity signifying that adsorption was physical [11].

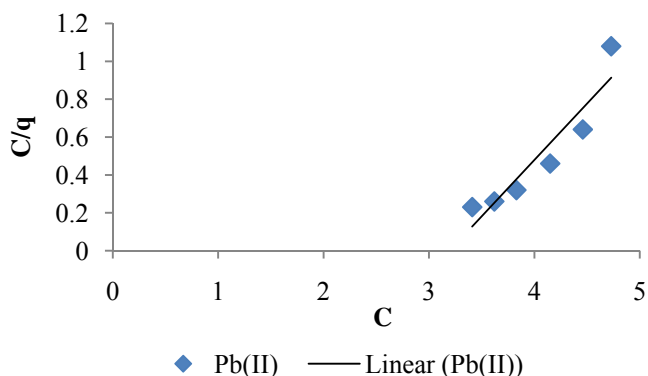


Figure 6. Langmuir isotherm plot for Pb (II)

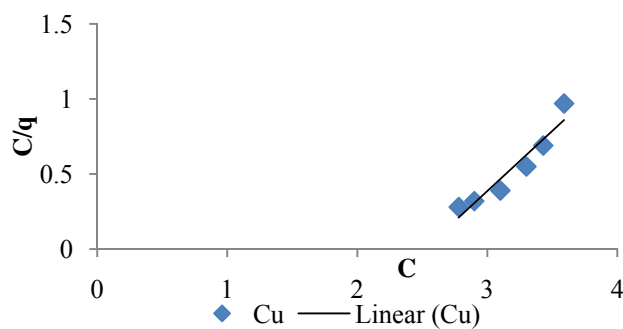


Figure 7: Langmuir isotherm plot for Cu (II)

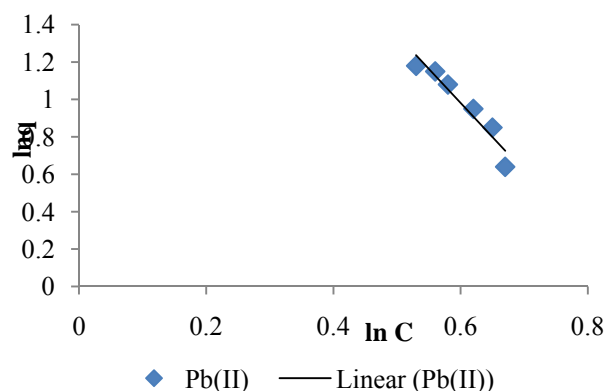


Figure 8 : Freundlich isotherm plot for Pb (II)

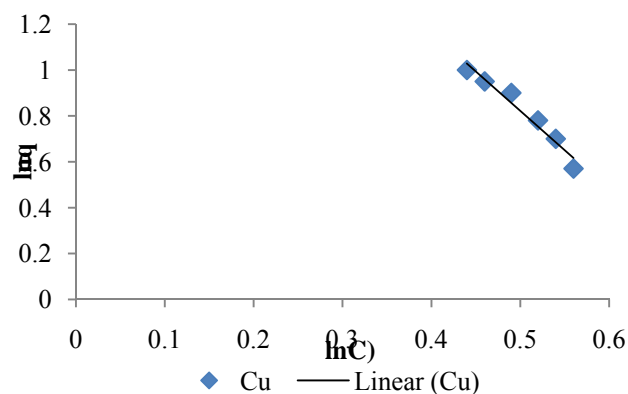


Figure 9: Freundlich isotherm plot for Cu (II)

4.6 Pseudo First Order Kinetic Model

The model is confirmed by a plot of $\ln(q_m - q_t)$ against t that is linear. From the plots in Figure 10 and Figure 11, it was observed that the relationship between metal ion diffusivity $\ln(q_m - q_t)$ and time is linear for all of the various temperatures (15, 25, 30, 45°C) and residence times (20, 40, 60, 80 and 120 minutes) indicating that the diffusivity of Pb(II) and Cu(II) onto AEP surface can be well described by the

pseudo-first order kinetic model. Because the adsorption was well described by the pseudo-first order kinetic model, further attempt of the second order kinetic model was not made.

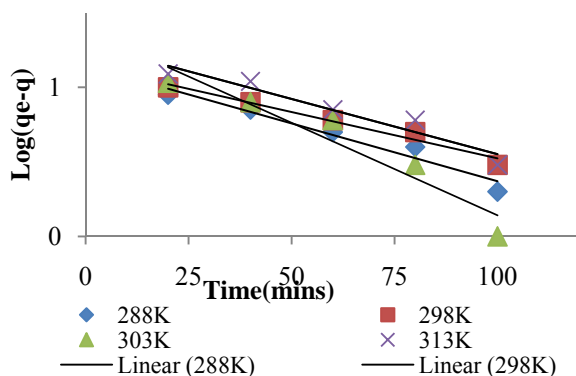


Figure 10. Pseudo-first order model plot for Pb (II) at varying temperature and residence time

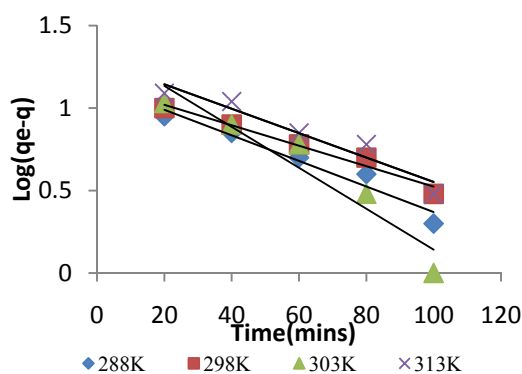


Figure 11. Pseudo-first order model plot for Cu (II) at varying temperature and residence time

Table 1: Linear langmuir isotherm parameters Pb (II) and Cu(II)

S/N	q_m	K_L	R^2	R_L
Pb(II)	0.83	0.51	0.873	0.38
Cu(II)	0.75	0.65	0.911	0.32

Table2: Freundlich isotherm models constants for Pb (II) and Cu(II)

Metal ion	n	K_f	$1/n$
Pb	0.37	3.43	2.70
Cu	0.29	4.05	3.45

5. Conclusion

The removal of Pb (II) and Cu (II) from aqueous solution using activated *egusi* peels (AEP) as bio-sorbent has been studied and found feasible. Though

increase in pH decreased adsorption, increase in other adsorption conditions such as temperature and adsorbent dosage was found to increase the adsorption of the two heavy metals significantly. The equilibrium data for Pb (II) and Cu (II) were well described by Langmuir and Freundlich isotherm models. Sorption of Pb (II) and Cu (II) was found favourable. The Freundlich model showed that the sorption mechanism was by physisorption. *Egusi* peels having been found as a good and inexpensive adsorbent could be utilized as a bio-sorbent for heavy metals removal from wastewater.

6. References

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