International Journal of Advanced Research in Chemical Science (IJARCS)
Volume 2, Issue 4, April 2015, PP 13-21
ISSN 2349-039X (Print) & ISSN 2349-0403 (Online)
www.arcjournals.org

The Kinetics and Equilibrium Studies of the Adsorption of (Cu^{2+}, Pb^{2+}) From Industrial Wastewater Using Rice Husk as Adsorbent

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Abstract: *Heavy metals have an adverse effect on the environment and these effects can be seen visibly on food, soil, climate, plants etc. Therefore, removal of heavy metals from industrial wastewater is primarily of importance. In the present study, the removal of heavy metals* **(Cu^{2+}, Pb^{2+})** *from the effluent from a textile industry was studied by adsorption technique using rice husk as adsorbent. The batch techniques was adopted under optimize condition of amount of adsorbent, time, and concentration using UV spectrophotometer. The concentration of heavy metals was measured before and after adsorption. The removal data were fitted into the Langmuir and freundlich isotherm equation. The value of their corresponding constant was determined. The pseudo-second-order rate equation as well as the micropore diffusion model described the kinetic data well. The study shows that about 90% of Cu^{2+} at 50mg/L and 65% of Pb^{2+} at 40mg/L was removed.The adsorption process was by a physical process (physiosorption).*

Keywords: *Adsorption, Efficiency Heavy metals, Physiosorption, Rice husk.*

1. INTRODUCTION

Heavy metals have adverse effect on the environment and these effects are visible on food, soil, climate, plants etc. Removal of heavy metals from industrial wastewater is primarily of importance, due to the serious environmental problem posed by the contamination of wastewater by heavy metals. Water is contaminated because of the indiscriminate discharge of wastewater containing heavy metals by small and medium scale industries which do not have the financial ability to provide conventional wastewater treatment method, which are quite expensive, leading them to dispose of their effluents in an inappropriate manner. The rate at which effluent from industries, are discharged into the environment especially water bodies have been on the increase as a result of urbanization (Abia and Igwe, 2006).

According to Blanco, et al., (2003), some conventional techniques which have been employed for the removal of metals from industrial wastewater include; precipitation, ion exchange, adsorption and electrolytic techniques, to mention a few. Heavy metals aside from their health effects are non-renewable resources. Effective recovery of heavy metals is therefore as important as their removal from waste streams.

Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants (Wang *et al.,* 2003). It has also been found to be superior to other technique for wastewater treatment when these terms are taken into consideration; initial costs, simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al,* 2004b). Adsorption however, has some limitations which include choice of adsorbents. In making a choice of what adsorbent to be used, factors such as availability, abundance, cost, regeneration ability have to be taken into consideration before a viable adsorbent is chosen.

Activated carbon is commonly used as an adsorbent in the purification of wastewater. This could be related to its extended surface area, high adsorption capacity, micro porous structure and special surface reactivity (Banat *et al.,* 2003). However, commercial activated carbon remains an expensive material. Igwe and Abia (2006), has proven beyond doubt that the use of bio-adsorbents can successfully replace the use of conventional adsorbents.

This has resulted in a search for low-cost material that can be used as alternative adsorbent materials.

Therefore, this research focuses on the applicability of rice husk as an adsorbent, suitable for the removal of heavy metals in effluent waste from the paint industry.

2. MATERIALS AND METHOD

2.1. Collection and Preparation of Adsorbent (Rice Husk)

The rice husk (*Oryzaglaberrima*) which was used as the adsorbent in this research was gotten from Lafenwa Rice Milling Market in Abeokuta, Ogun State, Nigeria. Upon collection, the rice husk was milled to a semi-powdered form. It was sieved through a 90µm-mesh sieve. It was then washed with distilled water till the color of the water was clear. After washing, it was dried in a hot-air oven at 60℃ for 24 hours (Vadilevan and Kumar, 2005).The dried materials were then soaked in 0.3M HNO_3 solution for 12 hoursand then washed with de-ionized water till a pH of 7 was obtained. It was then dried in an oven at 50℃ for 6 hours.

2.2. Effluent Sample

The wastewater for emulsion paint was obtained directly at the point of discharge and pH and temperature analysis were carried out immediately. The pH was found to be 9.9 (basic). It was stored at a temperature of approximately -10℃ till the point of use.100% effluent was prepared by pouring 100ml of effluent into a 1000L volumetric flask; subsequent dilution were carried out with it.

2.3. Sorption Experiments

2.3.1. Effect of Contact Time

Kinetic studies on the adsorption of the metalions from the aqueous solution were carried out by agitating 10ml of 100 mg/L standard metal ion solution of Cu^{2+} and Pb^{2+} with 0.025g of biomass in duplicates of five sample bottles to represent contact time of 5,10,15,20 and 30 minutes.The flasks were agitated in an isothermal water-bath shaker at 2800rpm and 30^{O}C for (5,10,15,20 and 30 minutes) at a fixed pH value of 7 until equilibrium was reached.

Aqueous samples were taken from the solutions and the concentrations were analyzed usingFlame Atomic Absorption Spectrophotometer. adsorption, qe (mg/g), was calculated by:

$$q_e = \frac{v\ (C_0 - C_e)}{m} \qquad (1)$$

Where, q_e = metal concentrated on the biomass mg (g biomass) at equilibrium

C_e = Metal concentrated in solution (mg/L) at equilibrium.

C_o = Initial metal concentrated in solution (mg/L)

V = Volume of initial metal solution used (L)

m = Mass of biomass used (g)

The Percentage Adsorption

The percentage adsorption was computed for each initial concentration using the equation;

$$\%\,adsorption = \frac{(C_e - C_0)}{C_0} \times 100 \qquad (2)$$

Where,C_e=The equilibrium concentration; C_o= The initial concentration.

2.3.2. Effect of Metal ion Concentration

Equlibrium sorption experiments for the metal ions were performedby adding 10ml of aqueous solutions (10, 20, 30, 40 and 50mg/L)of Cu^{2+} and Pb^{2+} ions to fixed mass of biomass (0.025g) and the resulting suspensions agitated for two hours, at pH 7 and room temperature. The metal ion contents were determined as described above.

2.3.3. Effect of Mass of Adsorbent

Another set of equilibrium sorption experiments were carried out with different weights of biomass (0.025,0.050,0.075,0.100 and 0.150g), to which 10ml of aqueous solution of fixed metal ion concentration (100 mg/L) and the suspension agitated for two hours.

3. RESULTS AND DISCUSSION

Table1. *Initial and Final conc. of Effluent samples under varying initial concentration*

Cu^{2+}				Pb^{2+}			
C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.
10	1.56	8.44	84.37	10	6.96	3.04	30.44
20	2.30	17.70	88.5	20	14.64	5.36	26.81
30	6.10	23.90	79.66	30	20.87	9.13	30.44
40	3.68	36.34	90.8	40	13.63	26.37	65.94
50	4.66	45.35	90.69	50	38.92	11.09	22.16

Table2. *Initial and Final concentration of effluent samples under varying adsorbent dose*

Adsorbent Mass	Cu^{2+}				Pb^{2+}			
	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.
0.025	100	26.80	73.20	73.20	100	37.73	62.27	62.27
0.050		18.80	81.20	81.20		68.09	31.92	31.92
0.075		12.42	87.58	87.58		73.82	26.18	26.18
0.100		6.00	94	94		96.45	3.55	3.55
0.150		0.01	99.9	99.9		100	-	-

Table3. *Initial and Final Concentration of Effluent samples under varying Contact Time*

Time (mins)	Cu^{2+}				Pb^{2+}			
	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.	C_0 (mg/L)	C_e (mg/L)	$C_0 - C_e$ (mg/L)	% Ads.
5	100	10.53	89.47	89.47	100	60	40	40
10		3.76	96.24	96.24		70.06	29.94	29.94
15		0.01	99.9	99.9		73.75	26.25	26.25
20		0.01	99.9	99.9		94.03	5.97	5.97
30		0.01	99.9	99.9		99.56	0.44	0.44

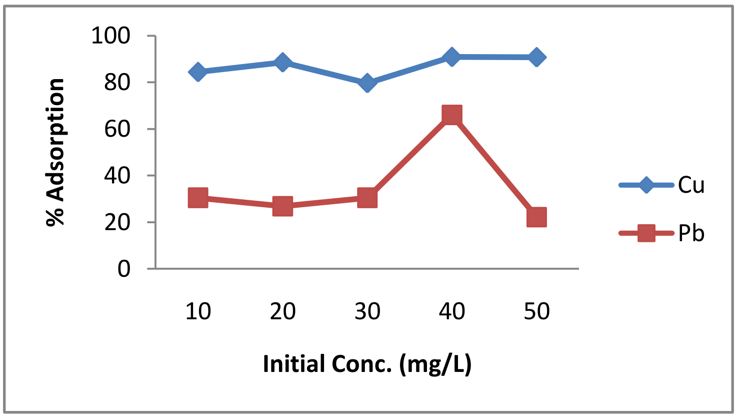

Figure1. *Plot of % Adsorption against Initial Conc. of Effluent Samples*

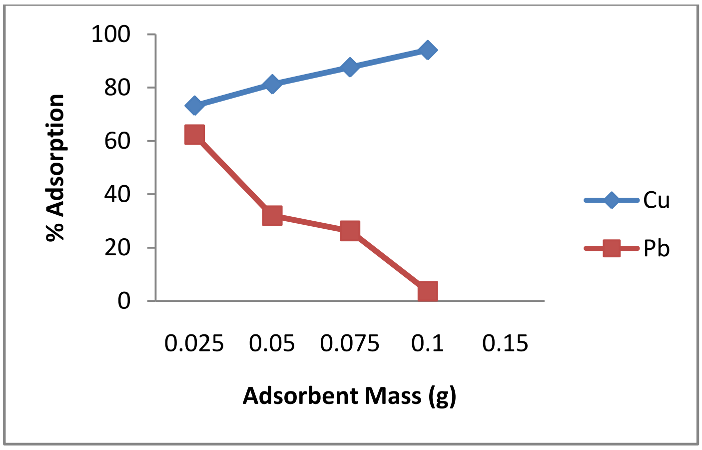

Figure2. *Plot of % adsorption against Adsorbent Mass*

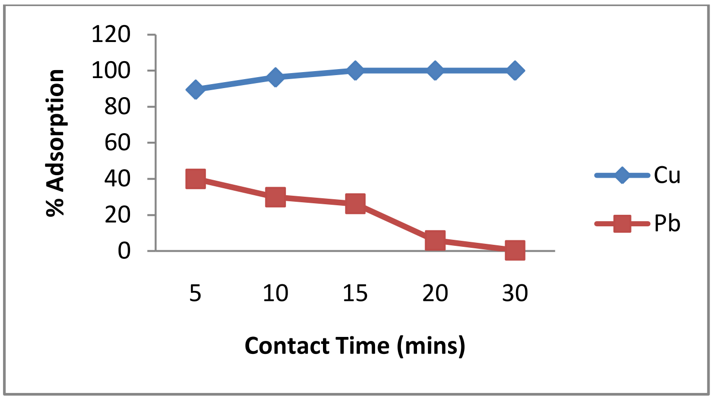

Figure3. *Plot of % Adsorption against Contact Time*

The removal of the Pb^{2+}ion in aqueous solutions and Cu^{2+} in effluent samples was found to increase with an increase in adsorbent mass. The increase in adsorption with increase in

3.1. Effect of Initial Concentration on Adsorption

Table 1 shows the initial and final concentration of the effluents samples at two hours, adsorbent mass (0.025g), pH (7.0) and temperature (31℃) .The effect of initial metal ion concentration on the sorption of Cu^{2+} and Pb^{2+} ions from theeffluent sample onto Rice husk biomass is shown in Figure1 above. The percentage removal of the metal ions from the effluent sample was found to increase steadily with increase in the initial metal ion concentration. The maximum adsorption (90.8%) at an initial concentration of 40mg/L was observed for copper ions and (64.94%) at 40mg/L for lead ions.

The decrease with initial concentration may be due to the fact that at lower concentration of metal ions almost all the active sites on the biomass are occupied and further increase in the initial metal ion concentration would only lead to supersaturation of biomass surface. Increase with increase in initial concentration implies that little of the metal ion were adsorbed at low concentration and sorption sites were still available.

3.2. Effect of Adsorbent dose

Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution (El-Said, 2010). Table 2 and figure 2 shows the initial and final concentration of the absorbate before and after the adsorption experiments under constant conditions of time (2 hours), C_o = 100mg/L, pH (7.0) and temperature (31℃).Adsorbent mass can be attributed to the availability of larger surface area and more adsorption sites. The % adsorption of Cu^{2+}ion was optimal at 0.15g of adsorbent. The removal of Pb^{2+} was found to decrease with increase in adsorbent mass. At very low adsorbent concentration, the adsorbent surface becomes saturated with the metal ions and the residual metal ion concentration in the solution is very large. The data clearly shows that rice husk is effective in the removal of Cu^{2+} from effluent samples than it is the other metal ion.

3.3. Effect of Contact Time

Table 3 and figure 3 show the initial and final concentration of the absorbate before and after the adsorption under constant conditions of concentration, adsorbent mass (0.025g), pH (7.0), varying time and temperature (31℃).The maximum adsorption was observed at 5 mins, with about 90% for Cu^{2+} and 40% for Pb^{2+} . The initial fast rate of metal sorption in the sample may be explained by the large number of sorption sites available at that time, after which the unsaturated sorption sites available are very few giving a decreasingly steady rate of adsorption. This behavior reflects the fact that the adsorption is a surface phenomenon and that the surfaces are readily accessible to the metal ions in the solution (Qinggi et al., 2004). It also suggests the occurrence of a rapid external mass transfer followed by a slower internal diffusion process which could be the rate determining step (Mohd et al., 2011). The slower internal diffusion process could be due to the slow diffusion of the adsorbed metals from the surface film into the micropores which are the least accessible sites for adsorption (Wong et al., 2003). This could also be due to the difficulty of metal ions to occupy the remaining vacant surface sites due to repulsive forces between metal ions and bulk phase (Bishnoi, 2003)

3.4. Kinetic Study

To analyze the mechanism of adsorption the data was fitted to various kinetic models such as pseudo- second order reaction and Intra-particle diffusion model. The Intra-particle diffusion model was employed to find out the rate controlling step in the process of adsorption of Pb^{2+} and Cu^{2+} onto rice husk.

3.4.1. Pseudo-Second Order Model

In an attempt to understanding the kinetic behavior of the sorption process of $Cu^{2+}$and Pb^{2+} on Rice husk biomass, the linear form of the kinetic rate expression model for a pseudo-second order reaction developed by Ho's was employed:

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} t \qquad (3)$$

Where,q_t= amount of divalent metal ion on the biomass surface (mg/g) at any time

q_e= amount of divalent metal ion sorbed at equilibrium (mg/g)

h_o = initial sorption rate

$h_o$is defined as; $h_o = k_2 {q_e}^2$

Where, k_2= pseudo-second order rate constant (g/mg min).

The model is represented by a plot of t\qt (mg/gmin^{-1}) against t (mins).

Table4. *Kinetic parameters from the Pseudo second order*

q_e (mg/g)	h_o (mg/g min^{-1})	K (g mg^{-1}min^{-1})
43.5	30.3	0.016
2.02	-0.290	-0.07

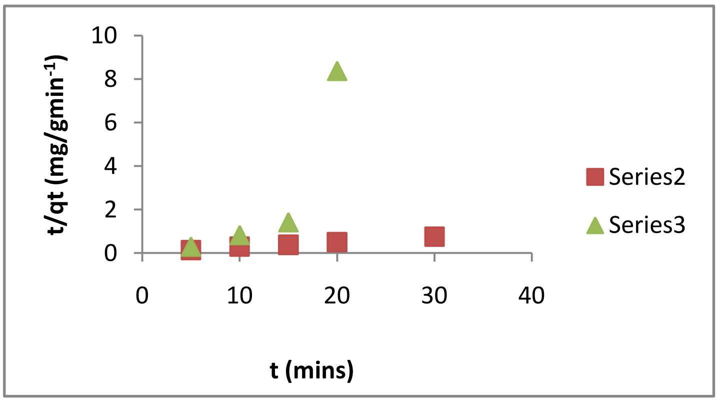

Figure4. *Pseudo-second order model for $Cu^{2+}$and Zn^{2+}*

3.4.2. Intra-particle Model (Weber-Morris)

Intra-particle diffusion is a transport process involving movement of species from the bulk of the solution to the solid phase. In a well stirred batch adsorption system, the intra-particle diffusion model has been used to describe the adsorption process occurring on a porous adsorbent. The structure of the solid and its interaction with the diffusion substance influences the rate of transport (Abdul rahman et al., 2010). The adsorbate transport from the solution phase surface of the adsorbent particles may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and the adsorption on the pore surface, or a combination of more than one steps. In a rapidly stirred batch adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption rate data. Generally, a process is diffusion controlled if it is dependent upon the role at which components diffuse towards one another. The possibility of intra particle diffusion was explored by using the intra particle diffusion model (Itodo et al., 2010). A plot of the amount of sorbate adsorbed, qt (mgg^{-1}) and the square root of the time, gives the rate constant (slope of the plot). It is calculated by using the intra particle diffusion model given below (Shrihari *et al.*, 2005);

$$q_t = k_{id}t^{0.5} + C_i \tag{4}$$

Where, k_{id} is the intra particle diffusion rate constant, C_i = intraparticle diffusion constant i.e. intercept of the line (mgg^{-1}). It is directly proportional to the boundary layer thickness.

It is assumed that the sorption mechanism is controlled by intra-particle diffusion if the following conditions are met:

- High R^2values to ascertain applicability
- Straight line which passes through the origin for the plot area qt vs. $t^{1/2}$.
- Intercept Ci < 0. A validity test which deviates from (ii) and (iii) above shows that the mode of transport is affected by more than one process (Hameed, 2009).

The deviation of the line from the origin further shows that intra-particle transport is not the only rate limiting step. Probably the transport of the sorbate through the particle-sample interphase onto the pores of the particles, as well as adsorption on the available surface of the adsorbent, is responsible for the adsorption. This is in line with the finding of Badmus *et al*., (2007).However, if the data exhibit multi-linear plots, two or more steps influence the absorption processes (El-said, 2010).

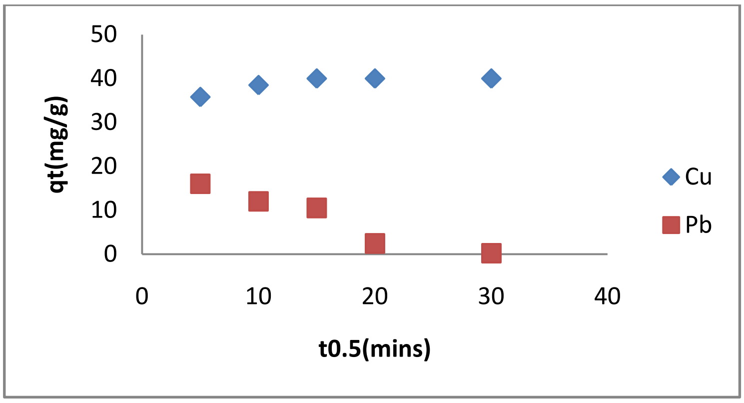

Figure5. *Intra-particle model plot of qt against* $t^{0.5}$ *for* Cu^{2+}*and* Pb^{2+}

Figure 5 reveal an initial linear step, corresponding to fast uptake of sorbate. The line in the initial stage does not pass through the origin which makes it worthy to note that uptake is dominated by film diffusion than it is by intra-particle diffusion process. In the third phase, diffusion remains fairly constant i.e. the pore volume is exhausted. Application of this model to experimental data gotten from effluent solution in this analysis gave a good fit plot for $Cu^{2+}$with a correlation coefficient of R^2 = 0.933 and a value of “a” which is less than unity (-0.23); also the intra-particle diffusion rate constant, $\boldsymbol{K_{id}}$is as high as 139. This translates to an enhanced rate of adsorption which is in turn, linked to improved bonding. (Otun et al., 2006).

It can be infered that intra-particle diffusion is not the sole rate controlling parameter. Probably the transport of the sorbate through the particle-sample interphase onto the pores of the particles, as well as adsorption on the available surface of the adsorbent, is responsible for the adsorption. This model has proved that Rice husk is a good material for fast and efficient sorption of Cu^{2+} ion but the process is much slower for Pb^{2+}. The adsorption was found to be dependent on contact time. The experiments show an enhanced rate of adsorption which is linked to improved bonding of the Cu^{2+} ions.

3.4.3. Langmuir and Freundlich Isotherm Model

Both Langmuir’s and Freundlich’s adsorption isotherm equilibrium models were used for the analysis of the metal-adsorbent system. Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between adsorbed molecules. Table 5 and fgure 6 and 7 shows the plots of 1/qe (g/mg) versus $1/C_e$ (L/mg) and $\log q_e$ (mg/g) versus Log C_e (mg/L), respectively.

The Langmuir linear equation below was used to calculate the maximum adsorption capacity of the adsorbent [18].

$$\frac{1}{qe}=\frac{1}{bqmaxCe}+\frac{1}{qmax} \qquad (5)$$

The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor (K_L) that can be defined by the following relationship [19].

$$K_L=\frac{1}{1+bCo}$$

Where C_o is the initial concentration (mg/L), while b is the Langmuir equilibrium constant (L/mg). The value of separation parameter K_L provides important information about the nature of adsorption. The value of K_L indicated the type of Langmuir isotherm to be irreversible (K_L=0), favorable ($0<K_L<1$), linear (K_L=1) or unfavorable (K_L>1). It can be explained apparently that when b > 0, sorption system is favorable [20].

The Freundlich isotherm is applicable to non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as [21]: the isotherm model proposes a monolayer sorption with a heterogeneous distribution of active sites, accompanied by interactions between adsorbed molecules.

$$\text{Log qe} = \log K_f + \frac{1}{n}(\log C_e) \qquad (8)$$

The adsorption constants (K_f and 1/n) were obtained by plotting log q against log C_e, the Freundlich isotherm parameter 1/n.

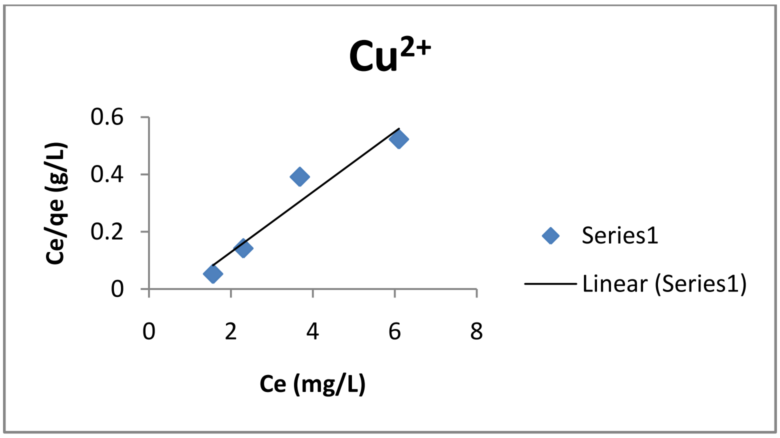

Figure6. *Langmuir isotherm for adsorption of* Cu^{2+}

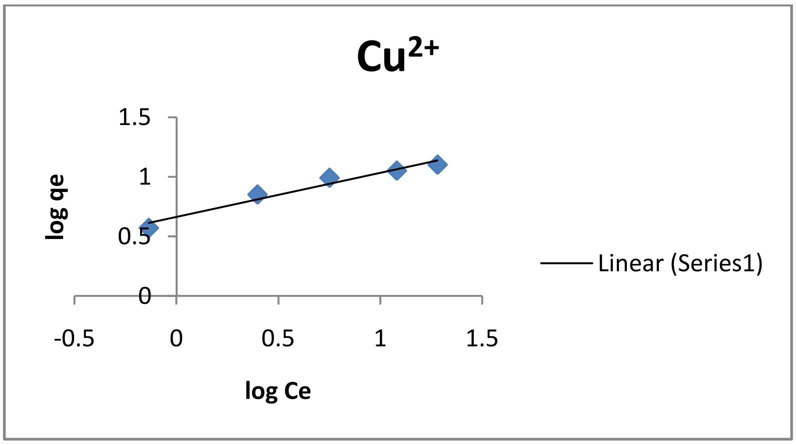

Figure7. *Freundlichisotherm for adsorption of* Cu^{2+}

Table5. *Langmuir and freundlichisotherm parameters for the adsorption of metal onto adsorbent*

	Langmuir			Freundlich	
	q_m (mg/g)	K_L ($dm^3 g^{-1}$)	R^2	$\frac{1}{n}$	K_f
Cu^{2+}	9.62	-1.3	0.93	0.71; n = 1.40	1.53
Pb^{2+}	0.27	0.57	0.83	1.14; n = 0.88	2.23

The results show that the sorption capacity of biomass towards Cu^{2+}andPb^{2+} is moderatelyhigh but higher for Cu^{2+}than Pb^{2+}.The differential sorption behaviour could be explained in terms of ionic radii of the metal ions: Pb^{2+} = 1.33A; Cu^{2+} = 0.81. Generally, the element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius. This may have influenced the greater sorption ability of Cu^{2+} on the biomass than Pb^{2+}.

The freundlich model was chosen to estimate the adsorption intensityof the sorbate surface.The Freundlich constant,$\mathbf{K_f}$, indicates the adsorption capacity of the adsorbent. The other Freundlich constant, n, is a measure of the deviation from linearity of the adsorption. If a value for n is equal to unity, this implies that adsorption process is chemical, but a value for n above unity indicates that adsorption is a physical process (Jiang et al., 2002).

In the sample, the value of $\frac{\mathbf{1}}{\boldsymbol{n}}$ is less than 1 for Cu^{2+} which suggest that the adsorption of Cu^{2+} is more favourably adsorbed unto Rice husk adsorbent surface. The values of $\frac{\mathbf{1}}{\boldsymbol{n}}$for Pb^{2+}found to be greater than unity indicate that the isotherm can be characterized by a convex Freundlich isotherm.This implies that significant adsorption of Pb^{2+}may take place from paint effluent sample even at high metal concentration. The high nvalue of Cu^{2+} (1.40), in relation to Pb^{2+}(0.88) and the high value of K_f for Pb^{2+}indicates the prefential sorption of Pb^{2+}. It also shows the ability of Rice husk biomass to remove these two metal ions from solution even at high concentrations. The Pb^{2+} ions (R^2 = 0.798) fit the Freundlich isotherm more than the Cu^{2+} ions (R^2= 0.705) and thus it can be employed in the study of adsorption of Pb^{2+} ions from the samples. The adsorption process of Cu^{2+} is proven to be an entirely physical process by the values of n (greater than 1).

4. CONCLUSION

Results obtained for the three critical examined conditions and from the mathematical kinetic models expression of the $Cu^{2+}$and Pb^{2+} onto rice husk, confirmed the good chemical reaction mechanism for the Ho-pseudo second-order and also equilibrium sorption Langmuir and Freundlich isotherm model fitted well. Meanwhile, this research work showed the excellent efficiency of the rice husk (*Oryzaglaberrima*) in removal of the two heavy metals from its aqueous solution. This also confirmed the importance, possibility and usefulness of known agricultural waste (*Oryzaglaberrima*) for the clean-up of heavy metals in industrial waste water.

ACKNOWLEDGEMENT

The author is grateful to the Bells University of Technology Ota Ogun State Nigeria for providing facilities for this research work.

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