

Kinetics and Isotherm Studies of Heavy Metal Removals from Electroplating Wastewater Using Cassava Peel Activated Carbon

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Abstract

Liquid waste discharged from process industries, when not correctly handled and disposed, poses a great threat to both man and the environment. In this work, the kinetics and isotherm studies of adsorption process of zinc, copper, lead and iron ions from electroplating wastewater using cassava peel activated carbon (CPAC) developed as an adsorbent were aimed. The important experimental factors of the process such as agitation time, adsorbent dosage, pH and agitation speed on the removal of the heavy metals were studied to optimize the adsorption capacity of zinc, copper, iron and lead using cassava peel activated carbon. The preliminary studies involving the factors were also used as the criteria for choosing the metals considered for the kinetics and the isotherm studies. The results obtained indicated that 2.0 g of adsorbent per 20 ml of waste water was enough to remove 70 % for Cu, 69.5 % for Zn, 81.3 % for Fe and 100 % for Pb, respectively from the wastewater after 60 minutes of agitation time. The optimum pH value was estimated to be 6. Considering the pseudo-first-order and pseudo-second-order kinetic models that were used to describe the kinetics data, the adsorption data were found to be better fitted with the pseudo-first-order kinetic model. Applying the experimental equilibrium data to Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models, their equilibrium parameters were determined and it was observed from the results that Freundlich isotherm model was able to fit the equilibrium data the best among the models considered because its square of correlation coefficient was the highest for each of the heavy metals considered in this work.

Keywords: Heavy metals, cassava peel activated carbon, adsorption isotherm, kinetic studies, isotherm studies.

1.0 INTRODUCTION

Industrialization is the back bone of every nation's economy and the enhancement of citizenry well-being. However the negative impacts of industrial developments especially in the developing countries have become sources of concerns. These industrial developments comes along with the generation of unwanted by-products, which in most cases are discharged into the ecological systems leading to different types of pollutions. Subsequent negative impact of such pollution is felt not only by human beings but also by living organisms including plants. For instance, the introduction of untreated effluents into rivers and water bodies leads to build-up of poisonous contaminants (water pollution) like heavy metals (Hg, Pb, Cu, Zn, etc.) among others. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Gupta and Sharma, 2001).

When heavy metals enter the food chain, they build up and cause mental retardation, reduction in haemoglobin, production and interference with normal cellular metabolism and consequently may damage the nervous system. Furthermore, strong exposure to heavy metals may cause gastric pain, nausea, vomiting, severe diarrhea, hemorrhage and affect the digestive tract and lungs (Klaassen *et al.*, 2001; Mohanty *et al.*, 2005). Thus, it is desirable to remove toxic heavy metals from wastewater, probably via adsorption process, before it is discharged into the environment.

One of the difficulties in describing the adsorption of heavy metals from waste streams is that wastewater contains more than one types of heavy metals. When several components are present, interference and competition phenomena for adsorption sites occur (Janget *et al.*, 2001; Abdullah, *et al.*, 2010). Study on palm kernel shell activated carbon has shown that competitive adsorption for active sites on the carbon surface resulted in a reduction of the overall uptake capacity of reactive dyes (Nourouzi *et al.*, 2009).

In this study, the adsorption process of a cassava peel activated carbon developed and used as low-cost adsorbent to remove zinc, copper, iron and lead from electroplating wastewater has been investigated by evaluating the environmental parameters affecting the adsorption process such as pH, agitation time, metal, adsorbent dosage and agitation speed and fitting the equilibrium adsorption data using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models

2.0 MATERIALS AND METHODS

2.1 Carbonization of Cassava Peel

The dried peels were crushed into powder form and 15 g of the samples were weighed into six different clean and pre-weighed crucibles, which were then introduced into the hot zone of a muffle furnace. The furnace temperature was increased at a rate of 10 °C/min from the room temperature. The peels were carbonized at different temperatures (250, 300, 350, and 400 °C). The samples were held at this temperature for various times (15, 30, 45, and 60 min) in order to establish optimum conditions. The content was then removed from the muffle furnace after the set period and

cooled in an open air for one hour. This process was repeated until a substantial amount of carbonized sample was obtained. Carbonaceous materials produced at different temperatures and time were then characterized.

2.2 Chemical Modification of Carbonized Materials

Activation of the carbonaceous material produced using zinc chloride and hydrochloric acid was carried out in accordance to the description reported by Yalcet *et al.*, (2000). Chemical activation using sulphuric acid was carried out using the method adopted by Kobya, *et al.*, 2005.

2.3 Effluent Collection

The raw effluent from an electroplating facility from a scientific development institute in Niger State, Nigeria was collected in a sterile 4 L plastic container from the point of discharge to the environment. For preservation, 5 mL of 2.0 M nitric acid was added per liter of the sample. The sample was refrigerated at approximately 4 °C to avoid any heavy metal precipitation and to allow the samples to be kept for further use (USEPA, 1979).

2.4 Heavy Metal Analysis

The effluent collected was analysed for presence of heavy metals (zinc, iron, copper and lead) by digesting 100ml of the effluent using 10 mL triple acid mixture (5:1:1 HNO₃:HClO₄:H₂SO₄) in a 250 mL conical flask placed in a fume cupboard (Momodu and Anyakora, 2010). The samples were covered properly with aluminium foil to avoid spillage and heated on a hot plate until the solution was reduced to 10 mL. The solution was then allowed to cool and it was made up to mark with distilled water before filtering into a 50 mL standard flask, labelled and ready for further analysis. The concentration of the heavy metals in the wastewater was determined using Atomic Absorption Spectrometer (Perkin, 210 vgp)

2.5 Adsorption and Kinetics Studies

The effects of some selected reaction parameters on the rate of adsorption of metal ions from the waste sample using activated cassava peel were investigated. The parameters considered included agitation time, adsorbent dosage, pH and agitation speed. To study the effect of agitation time on metal adsorption by cassava peel activated carbon (CPAC), 20 mL of the electroplating wastewater was transferred into sterile plastic bottles, covered and labelled accordingly. 1.0 g of the adsorbents were weighed into the labelled bottles and agitated for different contact time (15, 30, 45, 60 and 75 min). After each agitated time, the content of each bottle was filtered, and the equilibrium concentration of each of the metals in each filtrate was determined.

The effect of adsorbent dosage, that is, the amount of carbon on the adsorption of metals was studied by adding 20 mL each of the electroplating wastewater to various amounts of the adsorbent (1.0 - 2.0 g) in different plastic bottles. The bottles were covered and agitated on a mechanical shaker while keeping the equilibrium time and the pH constant.

To determine the effect of pH on the adsorption of metals, the pH of the wastewater was adjusted and maintained to the required value (2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) with a 1.0 M H₂SO₄ solution and mixed with the optimum weight of the adsorbents and agitated at a preset equilibrium time.

To study the effect of agitation speed, the optimal adsorbent dosage of the adsorbents was used to adsorb the heavy metals at different agitation speeds by adding the optimal dosages of the adsorbents to 20 mL of electroplating wastewater in different plastic bottles and agitated for 1 h. The agitation speed was adjusted from 150 rpm to 300 rpm and the content of each bottle was then filtered and analysed.

The adsorption capacity (q_e) was determined using the mass balance expression (Equation 1) (Horsfall *et al.*, 2004).

$$q_e = \frac{V(C_0 - C_e)}{M} \quad 1$$

The adsorption capacity (q_t) at time t was determined using Equation (2) (Demirbas *et al.*, 2004) given below.

$$q_t = \frac{V(C_0 - C_t)}{M} \quad 2$$

In the Equations (1) and (2), C_0 is the initial metal ions concentration, C_e is the concentration of metal ions in solution (mol/L) at equilibrium, C_t is the concentration of metal ions in solution (mol/L) at time t in solution, V is the volume of initial metal ions solution used (L) and M is mass of adsorbent used (g).

Kinetics of adsorption was studied by analyzing the adsorptive uptake of heavy metals from wastewater at different time intervals. The pseudo-first-order and pseudo-second-order model equations were fitted to model the kinetics of heavy metals adsorption onto the activated carbon produced. The linearity of each model, when plotted, was used to investigate the suitability of the model for the adsorption.

In this work, using the data generated from the experiments carried out, and considering the linearized forms of pseudo-first-order and pseudo-second-order reaction models given in Equations (3) and (4), respectively, the model parameters (k_1 and q_e for pseudo-first-order reaction model, and k_2 and q_e for pseudo-second-order reaction model) were estimated.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad 3$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad 4$$

Thereafter, with the data generated from the adsorption studies of the work, the parameters contained in Langmuir, Freundlich, Termkin and Dubinin-Radushkevich adsorption isotherms were also estimated using Equations (5), (6), (7) and (8), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad 5$$

$$q_e = k_f C_e^{\frac{1}{n}} \quad 6$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad 7$$

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \quad 8$$

3.0 RESULTS AND DISCUSSIONS

3.1 Heavy Metal Analysis

Industrial effluent discharge is recognized as one of the major sources of toxic chemicals in the environment. In the present study, metal ions contained in an electroplating effluent were removed using activated cassava peel carbon. In the first part of this study, after the collection of the wastewater, the effluent was analysed and shown in Table 1 below are the results of the analysis as well as the allowable limits of the heavy metals in wastewater. From the table, it can be seen that heavy metal analysis of the effluent sample has revealed the presence of Cu, Fe, Pb and Zn at various concentrations even beyond the permissible limits set by the regulatory authorities.

Table 1. Measured heavy metals concentration of the electroplating effluent

Metal	Effluent sample (mg/L)	Safe limit (mg/L)		
		FEPA (2001)	USEPA (1979)	FAO (1992)
Fe	16.6	0.30	0.30	-
Cu	43.5	0.01	1.00	0.2
Zn	17.4	5.0	5.0	2.0
Pb	0.005	-	-	-

3.2 Effect of Agitation Time on Adsorption of Heavy Metals

In this part of the work, an experiment was performed by adding 1g of CPAC to 20 mL of electroplating wastewater at constant temperature. The agitation speed was initially maintained at 100 rpm while the pH of the wastewater was 2.

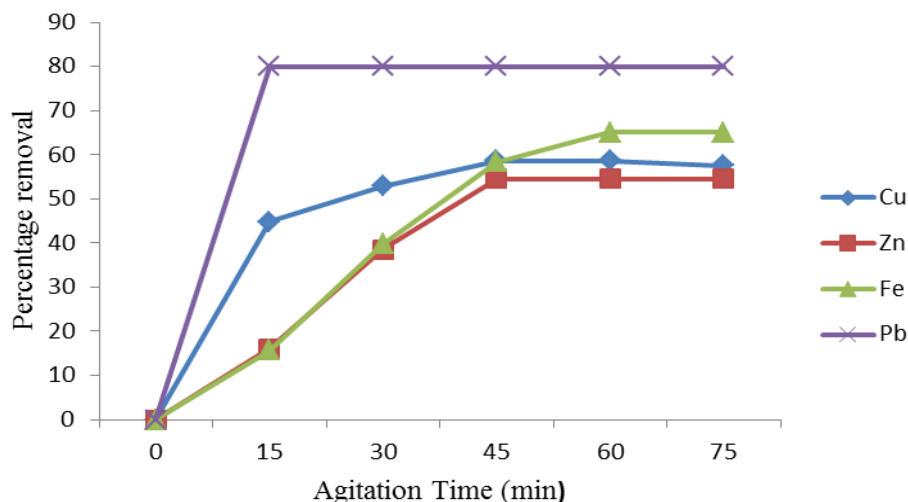


Figure 1: Effect of agitation time (15 min - 75 min) onto 1.0 g of cassava peel (CPAC) on the removal of heavy metals for 100 rpm agitation speed, and 298 K, pH = 2.

The result, as presented in Figure 1, indicated that the rate of adsorption increased significantly for some of the metal ions present in the electroplating wastewater between 15 – 60 min of the contact time. This result was found to be important because equilibrium time was one of the important parameters required for any economical wastewater treatment system. This trend was found to be in conformity with the observation made by Innocent *et al.* (2009). The rapid initial rate increase followed by a slow rate at a later period was attributed to the availability of excess adsorption sites on the adsorbents. The initial high adsorption rate was also discovered to be due to ion exchange followed by a slow chemical reaction of the metal ions with active functional groups on the sample, in line with what was reported in the work of Okuo and Oviawe (2007). As can be seen in the figure (Figure 1), the percentage adsorption remained constant after 60 minutes with comparatively low values (58.6%, 54.6%, 65.1%, and 80% for Cu, Zn, Fe and Pb, respectively). This was also seen to be due to the saturation of the adsorption sites after 60 min after which little or no increase in percentage adsorption was observed as contact time increased. CPAC was found to be efficient in the adsorption of most of the heavy metals considered. Mostly, or at times, the observable time for maximum adsorption was found to be between 60 - 100 min.

3.3 The Effect of Adsorbent Dosages

The effects of the adsorbent dosages used on the uptakes of the four heavy metals onto the adsorbent were studied at the optimized agitation time established using procedure stated earlier, and the results obtained are as presented in Figure 2.

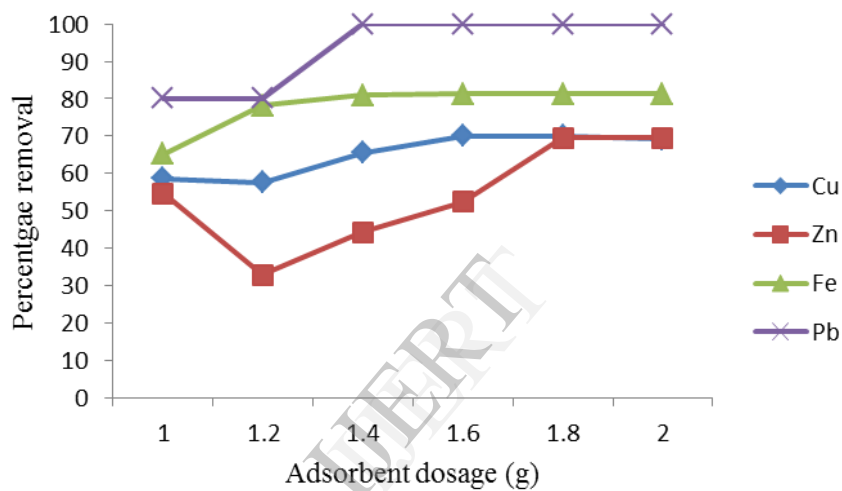


Figure 2: Effect of CPAC adsorbent dosage (1.0 - 2.0 g) on the removal of heavy metals for agitation speed = 100 rpm, and 298 K, pH = 2, agitation time = 60 min.

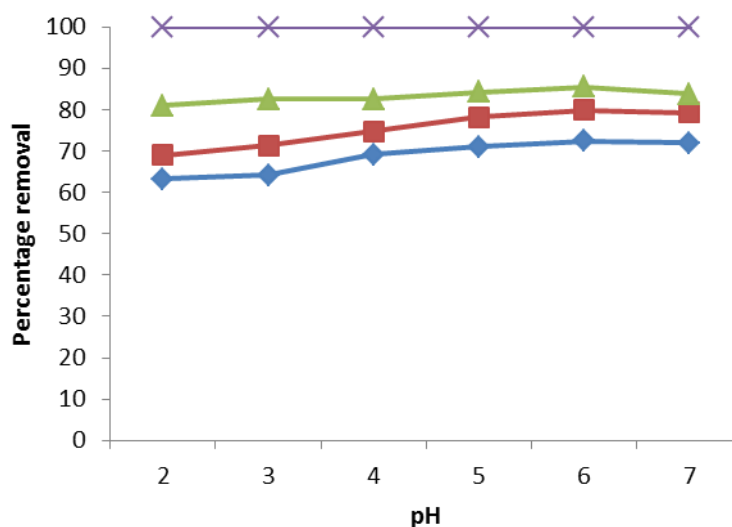


Figure 3: Effect of pH (2-7) onto 1.8 g of CPAC on the removal of heavy metals for agitation time = 60 min, 100 rpm agitation speed, and 298 K.

From Figure 2, it was revealed that heavy metal removal increases with increase in adsorbent. For the adsorbents, the removal remains unchanged after 2.0 g per 20 mL of adsorbent dosage for all the metal ions. The further increase in adsorption for Zn and Fe with adsorbent dosage was attributed to the availability of greater area and more adsorption sites. At adsorbent dosage < 1.8 g, the adsorbent surface became saturated with the ions and the residual ions in the electroplating wastewater was large. With increase in the adsorption dosage, the metal ions increased due to increased metal ion uptake by increased amount of adsorbent. At adsorbent dosage greater than 1.8 g, the increased ion removal became very low as surface metal ion and electroplating wastewater ions came in equilibrium with each other. At about 2.0 g, the removal efficiency became almost constant. Maximum removal of the heavy metals for CPAC was found to be 70 % for Cu, 69.5 % for Zn, 81.3 % for Fe and 100 % for Pb.

3.4 Effect of pH on Adsorption of Heavy Metals

The pH of the solution affects the surface charge of the adsorbent, as well as the degree of the ionization and speciation of different pollutants. A change in pH affects the adsorptive process through the dissociation of functional groups on the adsorbent surface active sites. In this work, the effect of pH was studied at room temperature by adjusting and maintaining the pH of the wastewater to the required value (2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) with a 1.0 M H_2SO_4 solution and mixed with the optimum weight of the adsorbents and agitated at a preset equilibrium time. The results obtained on the effects of pH on the quantity of heavy metal removals for CPAC are as presented in Figure 3. The figure revealed that the maximum uptake percentage of heavy metal removal was observed at pH = 6, while lead show no dependence on pH.

3.5 Effect of Agitation Speed on Adsorption of Heavy Metals

The effect of agitation speed was studied at room temperature (298 K), by adding the optimal dosage of the CPAC to 20 mL of electroplating wastewater in different plastic bottles while agitating for 1 h with the agitation speed being adjusted from 150 rpm to 300 rpm. The results obtained from the study involving the effect of agitation speed on the adsorption of heavy metals are as presented in Figure 4.

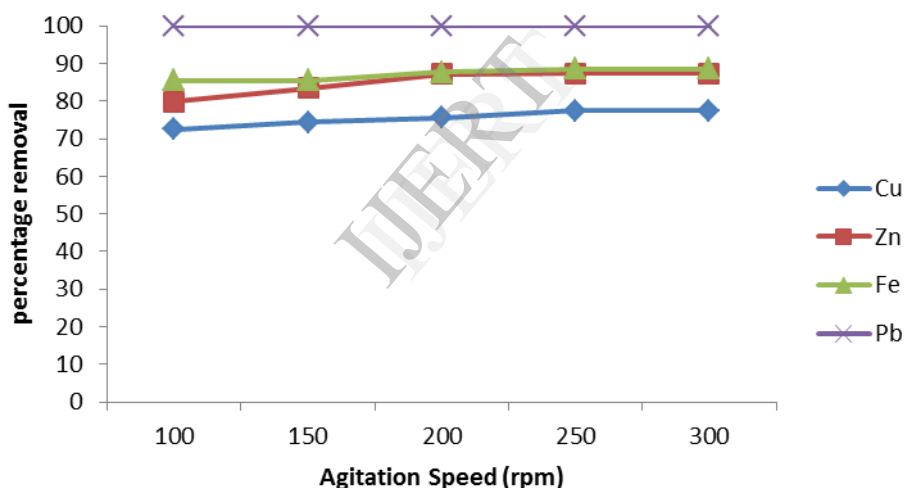


Figure 4: Effect of agitation speed (100-300 rpm) onto 1.8 g CPAC on the removal of heavy metals for 60 min agitation time, and 298 K, pH = 5.

Revealed from Figure 4 was that an increase in agitation speed from 100 to 300 rpm of the wastewater did not significantly increase the percentage removal of the metal ions, especially iron, copper, and zinc. Also, it was discovered that maximum recoveries for CPAC were obtained for all the three metal ions, with 98.1% removal of Fe(II), 99.7% of Cu(II) and 75.9% removal of Zn(II). In addition, Pb(II) was able to attain total removal of 100% even at a lower agitation speed of 100 rpm. The increase in agitation speed resulting to the significant increase in percentage removal of the zinc ions present in the wastewater was attributed to the fact that the increase in stirring rate was able to improve the diffusion of the metal ions towards the surface of the adsorbents and also reduce the film boundary layer surrounding the adsorbent, thereby increasing the external film mass transfer coefficient and the rate of metal adsorption.

3.6 Adsorption Kinetics

Adsorption is a mass transfer process that involves transfer of adsorbate from a liquid phase into a solid phase. The data obtained in this study as the dependence of adsorption capacity with time were used for kinetic analysis. The adsorption was carried out at the optimized conditions (adsorbent dosage: 1.8 g/20 ml; agitation time: 60 min, pH: 6, agitation speed: 250 rpm). Using the data obtained from the experiments carried out with copper, zinc and iron, noting that lead has been eliminated from further investigations owing to its nearly constant behaviour towards most of the

parameters investigated, the rate equations for the adsorption process were developed and shown in Figures 5 and 6 respectively are the results of the tests of pseudo-first-order rate equation (Lagergren Model) and pseudo-second-order rate equation (Ho Model) developed based on the adsorption of the further selected heavy metals (Cu, Zn and Fe) by the activated carbon developed from the cassava peel.

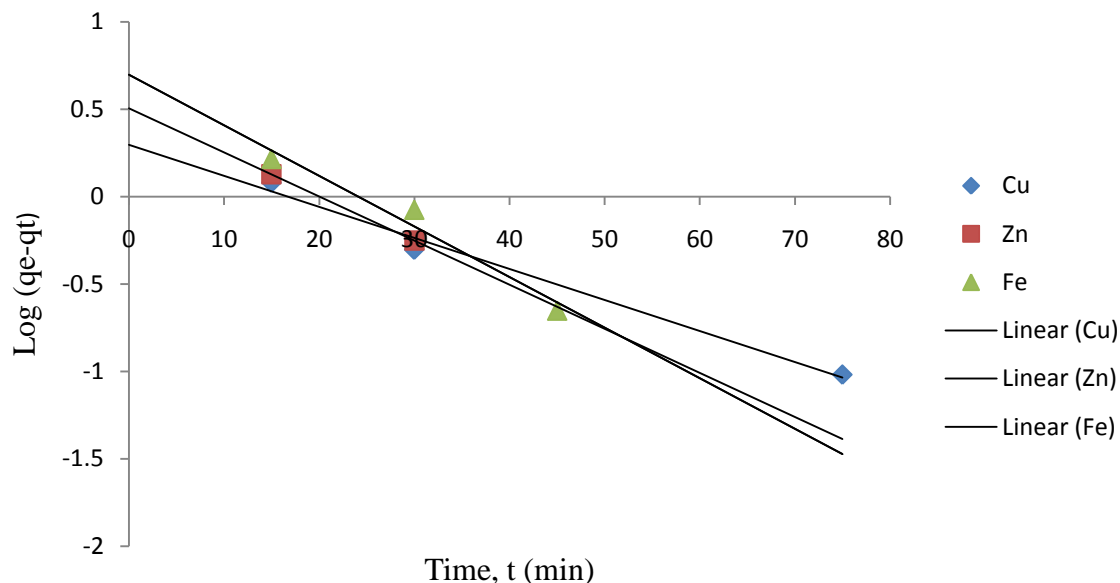


Figure 5: Pseudo-first-order reaction model for adsorption of heavy metals on CPAC

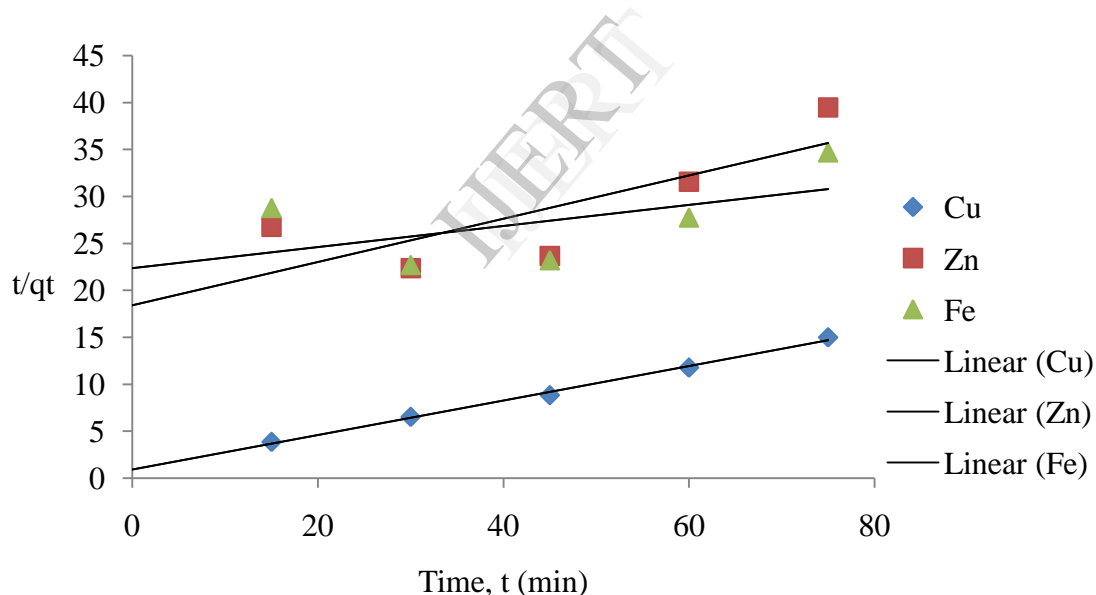


Figure 6: Pseudo-second-order reaction model for adsorption of heavy metals on CPAC

Table 2: Coefficient of Empirical Kinetic Models for CPAC

Adsorbent	Metal	Pseudo-first-order reaction model			Pseudo-second-order reaction model		
		k_1 (min^{-1})	R_1^2	q_e (mg/g)	k_2 $\text{gmg}^{-1} \text{n}^{-1}$	q_e (mg/g)	R_2^2
CPAC	Fe^{2+}	-0.06448	0.964	4.965	0.000561	8.929	0.301
CPAC	Cu^{2+}	0.039151	0.988	1.972	0.036048	0.036	0.996
CPAC	Zn^{2+}	0.057575	0.999	3.199	0.002875	4.347	0.619

It was discovered from the results of the fittings, carried out using Equations (3) and (4) for the pseudo-first-order and the pseudo-second-order reaction models, shown in Figures 5 and 6, respectively, that the pseudo-first-order reaction model (Lagergren Model) used yielded good straight lines for the copper, zinc and iron investigated compared to the pseudo-second-order reaction model, which was significantly scattered except for copper. Also, as given in Table

2, the squares of the regression correlation coefficients of the developed pseudo-first-order reaction models for the three metals were found to be very close to unity while for those (squares of the regression correlation coefficients) of the pseudo-second-order rate equation, it was only that of copper that was very close unity.

Thus, the valid applicability of the developed pseudo-first-order reaction model for the adsorption of heavy metals by the produced activated carbon from cassava peel has been well confirmed. Karthika, *et al.*(2010) reported similar results of kinetic studies when sago waste (prepared from cassava roots) was utilized as an adsorbent for the removal of heavy metals from aqueous solutions.

3.7 Adsorption Isotherms

Equilibrium analysis has been carried out on the data dependence of adsorption capacity to initial copper, zinc and iron concentration. The data were obtained from the adsorption of copper, zinc and iron from 20 mL of electroplating water using 1.8 g activated cassava char, CPAC at 60 min agitation time and pH = 5.

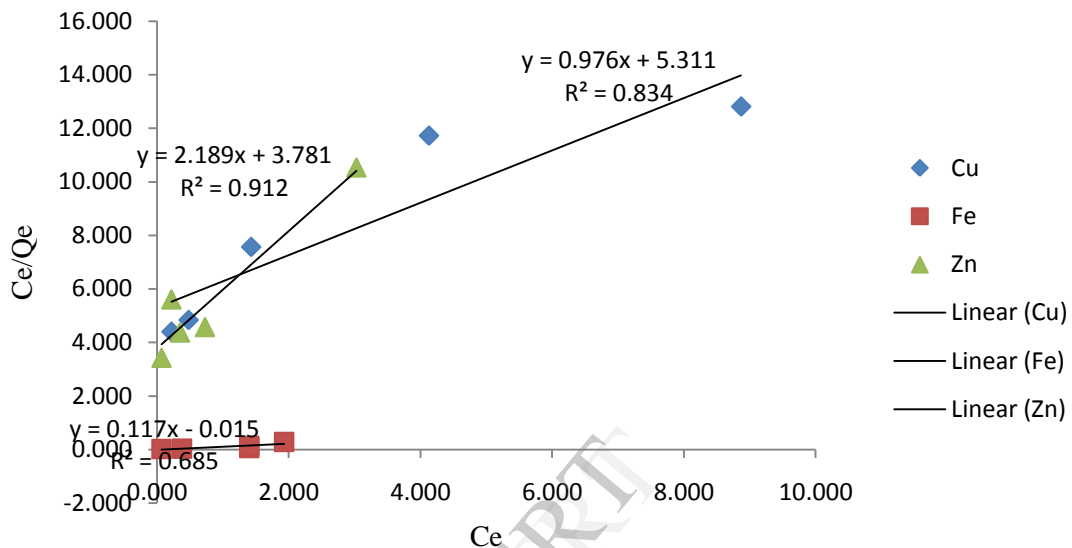


Figure 7: Langmuir adsorption isotherm for adsorption of heavy metals on CPAC

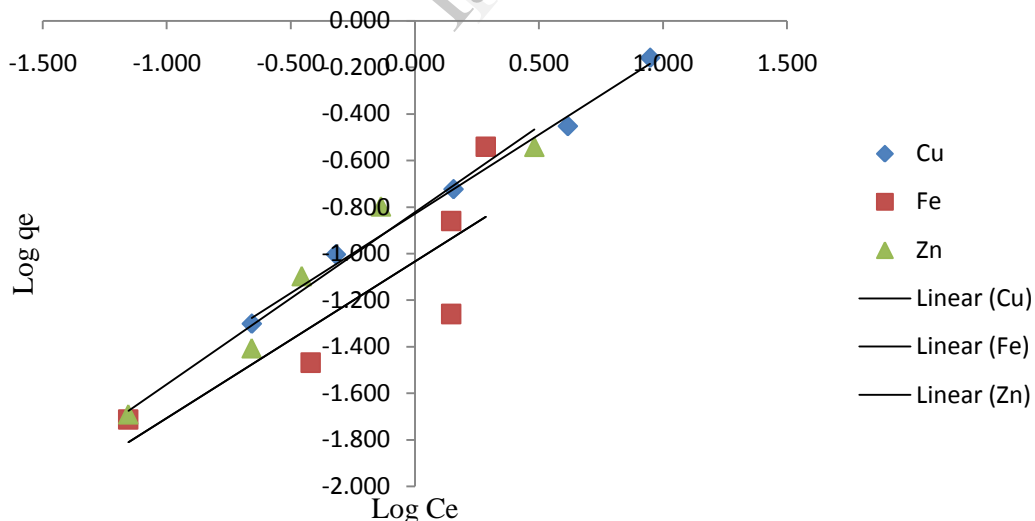


Figure 8: Freundlich adsorption isotherm for adsorption of heavy metals on CPAC

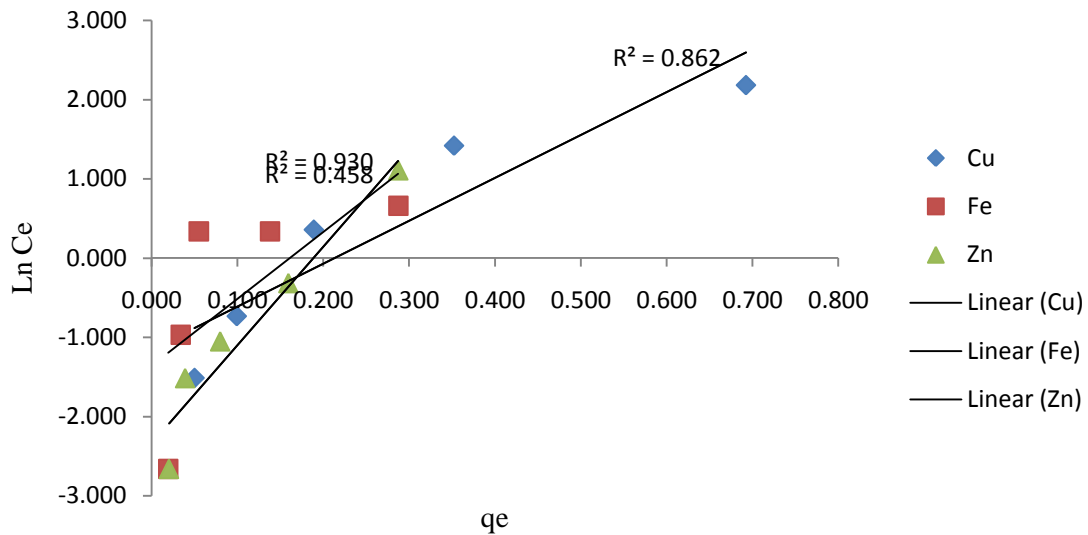


Figure 9: Temkin adsorption isotherm for adsorption of heavy metals on CPAC

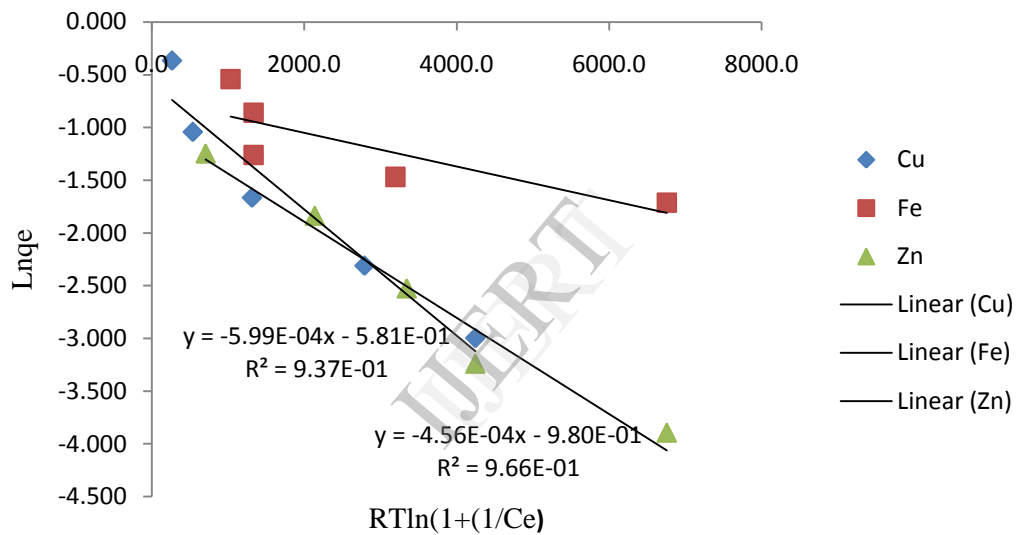


Figure 10: Dubinin-Radushkevich adsorption isotherm for adsorption of heavy metals on CPAC

Figures 7, 8, 9 and 10 respectively show the results of the fittings of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich to copper, zinc and iron uptake data onto CPAC. The results show that the four isotherm models described the partitioning between solid and liquid well by evaluating the maximum adsorption efficiency of the adsorbents. The model adsorption parameters and correlation coefficients are as given in Table 3.

Table 3: Isotherm model constants and correlation coefficients for heavy metals adsorption onto CPAC

Isotherm models	Constants	Unit	Value		
			Cu ²⁺	Fe ²⁺	Zn ²⁺
Langmuir	q _m	mgg ⁻¹	1.0245	8.5470	0.4568
	K _L	Lmg ⁻¹	0.1838	-7.8000	0.5789
	R ²	-	0.834	0.685	0.912
Freundlich	k _f	mgg ⁻¹	0.1483	0.0925	0.1507
	n	-	1.471	1.488	1.355
	R ²	-	0.994	0.735	0.958
Termkin	K _T	Lmg ⁻¹	1.3962	11.3127	11.4730
	B	-	15582.214	45880.963	33034.293
	R ²	-	0.862	0.458	0.930

Dubinin-Radushkevich	E	KJmol ⁻¹	28.8916	56.0772	33.1133
	q _D	mgg ⁻¹	0.5593	0.4804	0.3753
	B	mol ² KJ ⁻²	0.000599	0.000159	0.000456
	R ²	-	0.937	0.667	0.966

Adsorption isotherm model parameters estimated using the expressions given in Equations (5), (6), (7) and (8) for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption models respectively were reported in Table 3. It was discovered that the values of the Langmuir constant, q_m , computed which were obtained to be 1.0245, 8.5470 and 0.4568 mgg⁻¹ indicated that its adsorption was the best at low concentration of Cu²⁺, Fe²⁺, and Zn²⁺ compared to those obtained from Freundlich constant, K_f , which were 0.1483, 0.0925 and 0.1507 mgg⁻¹, and Dubinin-Radushkevich constant, q_D , which were 0.5593, 0.4804 and 0.3753 mgg⁻¹, respectively for Cu²⁺, Fe²⁺, and Zn²⁺. However, considering the square of the correlation coefficients (R²), it was observed that the results fitted best with Freundlich model among all the models considered. In addition, the Freundlich constant, n, which was estimated to be greater than 1 also confirmed its adequacy for describing the adsorption of heavy metals from the electroplating wastewater using cassava peel activated carbon.

4.0 CONCLUSIONS

The results obtained from this work have revealed that between the two kinetic (pseudo-first-order and pseudo-second-order) models analysed for the adsorption of copper, zinc, lead and iron ion from electroplating wastewater onto the surface of the developed cassava peel activated carbon, pseudo-first-order model was found to represent the process better. Furthermore, considering the four isotherm models that were used to fit the equilibrium data generated from the process, Freundlich isotherm model was discovered to best because of its very high square of correlation coefficients for the three heavy metals considered.

NOMENCLATURES

b	Langmuir constant (energy of adsorption) (L/mg)
C _e	Concentration of metal ions in solution (mol/L) at equilibrium,
C _o	Initial metal ion concentration (mol/L)
CPAC	Cassava peel activated carbon
C _t	Concentration of metal ions in solution at time t (mol/L)
FAO	Food and Agriculture Organization
FEPA	Federal Environmental Protection Agency
k ₁	Adsorption rate constant of pseudo-first-order kinetic model (min ⁻¹)
k ₂	Adsorption rate constant of pseudo-second-order kinetic model (g mg ⁻¹ min ⁻¹)
K _f	Freundlich constant related to adsorption capacity
K _L	Constant related to the affinity of the binding sites and energy of adsorption (L/mg)
K _T	Temkin equilibrium binding constants corresponding to the maximum binding energy (L/mg)
M	Mass of adsorbent used (g)
n	Freundlich constant related to adsorption intensity
q	Amount of heavy metal ions adsorbed at time t, mgg ⁻¹
q _D	Adsorption capacity (mg/g)
q _e	Amount of heavy metals adsorbed at equilibrium time mgg ⁻¹
q _m	Langmuir constant (adsorption capacity) (mg/g)
R	Universal gas constant (Jmol ⁻¹ K)
T	Absolute temperature (K)
t	Time, min
USEPA	United States Environmental Protection Agency
V	Volume of initial metal ions solution used (L)
ε	Polanyi potential

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