ADSORPTION CHARACTERISTICS AND MECHANISMS OF PLANTAIN PEEL CHARCOAL IN REMOVAL OF CU (II) AND ZN (II) IONS FROM WASTEWATERS

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ABSTRACT

The effects of pH, contact time and temperature on the ability of plantain peel charcoal to remove Zn^{2+} and Cu^{2+} from synthetic wastewaters were investigated. The charcoal used as the adsorbent was prepared from unripe plantain peels. The adsorption process established pH 5 and pH 9 as the respective optimal working pH values for Zn^{2+} at 30°C and Cu^{2+} at 40°C. Changes in enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) were also determined. Data evaluation showed that the adsorption of Zn^{2+} and Cu^{2+} followed the pseudo-second order adsorption kinetic model with the Langmuir model being the best fit for the isotherm model. The thermodynamic study revealed that the adsorption was a physisorption process which was spontaneous and endothermic in nature. It was concluded that plantain peel charcoal could efficiently serve as an alternative low cost adsorbent for the removal of heavy metal ions from wastewaters.

Keywords: Adsorption, Heavy Metals, Thermodynamics, Charcoal, Wastewater.

INTRODUCTION

Problems associated with gross contamination of the environment including water bodies by various toxicants have continued to attract the global attention of the stakeholders both in the private and public sectors. The discharge of untreated industrial effluents and sewage from metabolic wastes produced by humans and other organisms into water bodies especially in the developing countries has been on the increase for three major reasons. Firstly, there has been a steady increase in the urbanization and industrialization trend around the world with more pollutants being released into the environment. Secondly, many developing nations find it difficult to afford the state-of-the-art technology for wastewater treatment such as obtained in the developed nations. Also, the level of awareness about how to manage and sustain the environment is still very low in the developing countries (Oluyemi *et al.*, 2008).

Some of the pollutants released into the environment contain chemicals such as heavy metals, pesticides, volatile organic compounds and dyes, many of which are toxic to human and aquatic lives (Blaise *et al.*, 2000). The major sources of heavy metals are textile and dye, electroplating, solder, battery, pigment and paint, plastics and metallurgical industries. Though both Cu and Zn are essential elements, their excessive ingestion can cause vomiting, nausea, stomach cramps, skin irritations, convulsions and in some cases, may lead to death (Paulino *et al.*, 2006; Oyaro *et al.*, 2007).

Activated carbon or charcoal is used widely to treat wastewater to remove organic or inorganic pollutants and heavy metals because of their large specific surface area, high adsorption capacity and special surface chemical properties (Park and Kim, 1999; Ekebafe *et al.*, 2010). Activated carbon has been prepared from various raw materials which have high carbonaceous materials. These include maize cob, wood, plantain peel, saw dust, bone, coconut shell, coir pith, nut shells, almond shells, peanut husks (Ferro-Garcia *et al.*, 1988; Cheung *et al.*, 2001; Ricordel *et al.*, 2001; Rao *et al.*, 2006; Oluyemi *et al.*, 2009; Ekebafe *et al.*, 2010; Ewansiha *et al.*, 2010). Plantain peel is particularly abundant and can readily be obtained from dump sites, local farmers and traders in the tropics because plantain is a widely cultivated food crop in countries within the West African sub-region. In addition, the production of charcoal from it is less time consuming and requires less energy when compared to production of charcoal from materials such as bones and woody materials (Oluyemi *et al.*, 2009).

Oluyemi *et al.* (2009) studied the efficiency of charcoals generated from cocoa pod, bamboo, plantain peel and maize cob in removing heavy metals from wastewaters. It was established that of the four adsorbents produced from agricultural wastes, charcoal from plantain peel gave the best adsorption performance. However, the study did not go further to establish the mechanism by which plantain peel charcoal adsorbed heavy metal ions from wastewaters. Thus, the present study was designed to investigate the kinetics, equilibrium and thermodynamics of Zn^{2+} and Cu^{2+} removal from synthetic wastewater using plantain peel charcoal. The understanding gained from the study would reveal the adsorption mechanism by which such heavy metal ions could be removed from wastewaters. This, in turn, could enhance the technological applicability of plantain peel charcoal by developing countries as a viable and an affordable alternative to the hi-tech adsorption procedures available in the developed countries in wastewater control and management. In addition, finding an alternative use for plantain peels which occur as part of huge agricultural wastes in many tropical countries would mean creating a cleaner environment.

EXPERIMENTAL
Preparation of Charcoal
Preparation of the charcoal used as adsorbent was done by subjecting unripe plantain peels to incomplete combustion as described by Oluyemi *et al.* (2009). Unripe plantain peels were cut into pieces, rinsed thoroughly with distilled water to remove debris and other impurities. The plantain peels were dried in an oven to a constant weight at a temperature of 105°C. The oven dried plantain peels were carbonized in an earthenware pot, covered and heated at a high temperature. The pot content was stirred occasionally to ensure uniformity of temperature and consequent transformation of the plantain peels into charcoal. Complete combustion of the peels was prevented by covering the pot content leaving only a small aperture to serve as a vent. The charcoal formed was allowed to cool in a desiccator before it was ground using an agate mortar and pestle to increase the surface area of absorption. The powdered charcoal was sieved using a sieve of 500 microns pore size. Activation of the sieved charcoal was achieved by soaking the charcoal in

0.2 M sulphuric acid for 48 hours. The charcoal was filtered, rinsed thoroughly with doubly distilled water and dried for about 12 hours at 130ºC in a Gallenkamp Oven (Model Ov-160, England).

Sterilization of Apparatus
The glassware used, including measuring cylinders, volumetric flasks, beakers, conical flasks, watch glass and sample bottles (polyethylene containers) were soaked in detergent solutions overnight. They were thereafter washed thoroughly with hot liquid detergent solutions, and then rinsed properly with distilled water. The washed polyethylene sample bottles were further soaked in 10% HNO_3 for 48 hours and subsequently rinsed with distilled water. A mixture of acetone and n-hexane was used to further rinse the apparatus. This step was necessary to remove any trace organic contaminants such as grease that might adhere to the walls of the apparatus. Such organic contaminants could harbour some trace metals if not properly removed. All the chemical reagents used were of analytical grade.

Preparation of Synthetic Wastewater
A 1000 $mg.L^{-1}$ stock solution of Zn^{2+} and Cu^{2+} mixture was prepared with doubly distilled water from nitrates of Zn and Cu. From these, dilution was done to obtain the 50 $mg.L^{-1}$ working synthetic wastewater solution. Fresh dilutions of the stock solution were prepared for each adsorption study. The solutions were adjusted to the appropriate pH values using buffer solutions.

Adsorption Studies
The adsorption studies were carried out by contacting 1.5 g of the charcoal with 200 mL of the 50 $mg.L^{-1}$ metal ions solution mixture in a beaker. Starting from 10°C, gentle stirring and mixing of the adsorbent and wastewater was done by means of a mechanical stirrer for 20 minutes in a thermostated water bath. The charcoal was filtered from the solution using Whatman No. 42 filter paper. This process was repeated for similar solutions at 40, 60, 80, 100, 120, 140, 160 and 180 minutes, respectively.

Adsorption studies were carried out at pH 3, 5, 7 and 9 in order to investigate the effect of pH on

the adsorption behaviour of Cu^{2+} and Zn^{2+}. This is the common pH range within which industries discharge effluents into the environment (Oluyemi et al., 2009). The pH at which maximum adsorption occurred was established at 30 and 40°C. Also, the effects of contact time and temperature were studied at the pH of maximum adsorption at temperatures 10, 20, 30, 40 and 50°C for time intervals of 20 minutes within the range of 0 and 180 minutes.

Quantification of Heavy Metals in the Solutions

The initial and residual metal ion concentrations in the supernatant solution were determined using Flame Atomic Absorption Spectrophotometer, FAAS, (Buck Model 205 FAAS, East Norwalk, USA). The amount of metal ions adsorbed for each parameter was determined by the difference between the initial metal ion concentration and the concentration of metal ions in the supernatant solutions. Each determination was done in triplicate and the mean value for each experiment was calculated and presented. A blank experiment was conducted by analyzing doubly distilled water to establish blank level.

The adsorption capacities, q_e and q_t, which represent the amounts ($mg.g^{-1}$) of metal ions adsorbed by the adsorbent at equilibrium and at time t, respectively, were calculated by the following equations:

$$q_e = \frac{(C_o - C_e)}{M}V \qquad (1)$$

$$q_t = \frac{(C_o - C_t)}{M}V \qquad (2)$$

where C_o, C_e, and C_t are the initial concentration ($mg\ L^{-1}$) of metal ion in solution, the final concentration ($mg\ L^{-1}$) of metal ion in solution at equilibrium, and the final concentration ($mg\ L^{-1}$) of metal ion in solution at time, t, respectively; V is the volume (L) of solution and M is the mass (g) of adsorbent.

The results were also expressed as the percentage removal (R_p) of the metal ions from solution by the plantain peel charcoal using the equation below:

$$R_p(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

Adsorption of Cu^{2+} and Zn^{2+} at various pH

Figure 1 shows the adsorption plots for the effect of pH on the removal of Cu^{2+} and Zn^{2+} from synthetic wastewater. Figure 1(a) present adsorption of Zn^{2+} onto adsorbent at various pH and temperatures. For Zn^{2+}, the adsorption capacity increased with increase in pH of the solution as observed by Chirenje et al. (2005), Mahmoodi (2011), until it got to pH 5 when a maximum of 91.17% Zn^{2+} was removed from the synthetic wastewater.
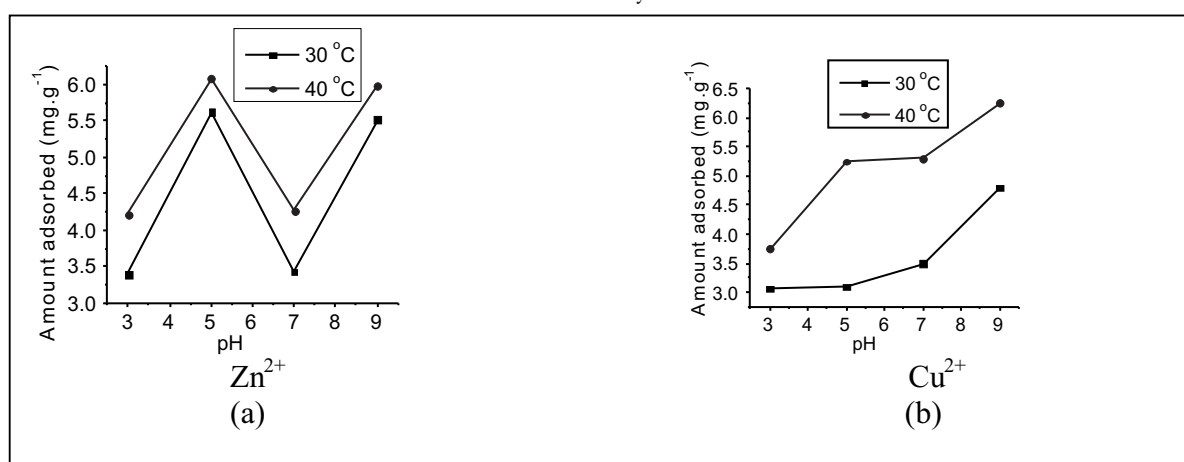

Figure 1: Adsorption of Zn^{2+} and Cu^{2+} onto Plantain Peel Charcoal at Various pH and Temperature
(a) Adsorption of Zn^{2+} onto Plantain Peel Charcoal at Various pH and Temperature
(b) Adsorption of Cu^{2+} onto Plantain Peel Charcoal at Various pH and Temperature

After this, there was a decrease until pH 7 was attained, and then, an increase between pH 7 and pH 9. At lower pH than 5, there probably was more vigorous competition between the Zn^{2+} and H^+ ions in solution for the active sites on the adsorbent (Hamdaoui and Chiha, 2007). This could be because as the pH increased, there was an increasing negative charge density on the adsorbent (Olayinka *et al.*, 2007) amounting to a decrease in hydrogen ions and consequently, less competition for the active sites, and hence, more metal ions adsorption. The apparent increased adsorption of Zn^{2+} at pH 9 during which 89.82% Zn^{2+} was removed was likely due to formation and precipitation of hydroxides of these metals (Olayinka *et al.*, 2007). In the case of Cu^{2+}, there was a progressive adsorption and removal from the synthetic wastewater until a maximum removal amount of 93.83% took place at pH 9. This result agreed with the ones obtained by earlier workers

(Oluyemi *et al.*, 2009). It could be inferred that Cu^{2+} removal from the waste water was by both adsorption and precipitation phenomena. The removal of the two ions from the synthetic wastewater was more efficient at a relatively higher temperature.

Effects of Contact Time and Temperature on Adsorption of Cu^{2+} and Zn^{2+} onto Plantain Peel Charcoal

Figure 2 shows the effect of time and temperature on the adsorption of Zn^{2+} and Cu^{2+}. Figure 2(a) presents the effect of time and temperature on the adsorption of Zn^{2+} and Figure 2(b) presents the effect of time and temperature on the adsorption of Cu^{2+}. The adsorption capacity increased with increase in contact time as shown in Figure 2. The adsorption was observed to be rapid initially and then became slower.
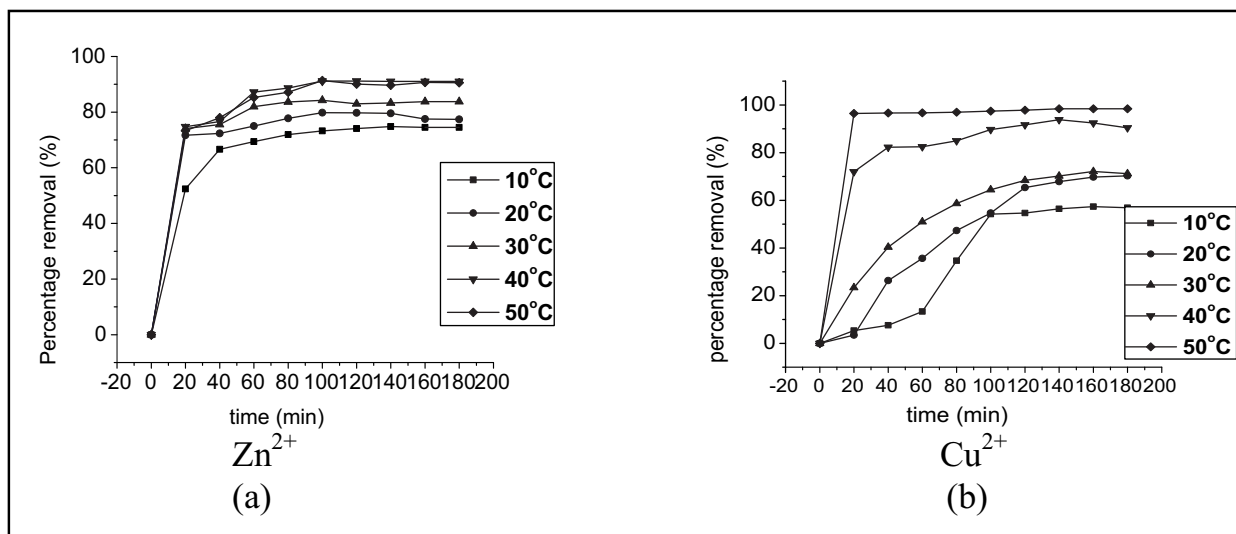

Figure 2: Effect of Time and Temperature on the Adsorption of Zn^{2+} and Cu^{2+} on Plantain Peel Charcoal
(a) Effect of Time and Temperature on the Adsorption of Zn^{2+} onto Plantain Peel Charcoal
(b) Effect of Time and Temperature on the Adsorption of Cu^{2+} onto Plantain Peel Charcoal

This can be attributed to the strong attractive forces between the metal ions and the adsorbent at the beginning (Hamdaoui and Chiha, 2007) which began to slow down due to gradual saturation of the adsorbent surface. The adsorption of Zn^{2+} reached equilibrium after 140 minutes at 10°C, while at higher temperatures of 20 to 50°C, the equilibrium was attained after 100 minutes. For Cu^{2+}, equilibrium was attained after 160 minutes at

10°C but at higher temperatures of 40 and 50°C, equilibrium occurred after 140 minutes. Zn^{2+} was more rapidly adsorbed than Cu^{2+}. That is, Zn^{2+} had greater affinity to be adsorbed by plantain peel charcoal than Cu^{2+}. The relationship between the percentage removal of the metals and time was both linear and exponential. This could be as a result of combination of factors such as solute - solute competition, the interaction between the

solute and the surface of the adsorbent, hydration capacity, pH and number of sites that are available (Oke *et al.*, 2011).

It was noticed that as the temperature increased, the uptake of the metals from the synthetic wastewater also increased (Figure 2), which implied that mobility of metal ions increased thus causing more frequent collisions between metal ions and the surface of the adsorbent (Hamdaoui and Chiha, 2007).

Adsorption Kinetics of Zn^{2+} and Cu^{2+} onto Plantain Peel Charcoal

To investigate the kinetics of adsorption of the metal ions, the adsorption data were applied to the pseudo-first order, pseudo-second order, and intraparticle diffusion. The pseudo-first order kinetic equation (Lagergren, 1898) used is:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{4}$$

where q_t and q_e (mg.g^{-1}) are the amounts of metal ion adsorbed at time t (min) and equilibrium respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first order kinetics. After integration and applying boundary conditions, t = 0 to t = t, and q = 0 to $q = q_e$, the equation becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

Linear plots of $\ln(q_t - q_e)$ against t gives a slope of k_1 and an intercept of $\ln q_e$ from which q_e can be calculated. The rate constants and the values of correlation coefficient are presented in Table 1 from which it can be seen that the adsorption of

Zn^{2+} and Cu^{2+} did not comply with the pseudo-first order model. Thus, the pseudo-second order equation used (Ho and Mackay, 1999) stated:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

where k_2 (g.mg^{-1}min^{-1}) is the rate constant of pseudo-second order equation.
Upon integration and linearization by applying boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, it becomes\

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

The values of eq and k_2 were calculated from the slope and intercept of a linear plot of t/q_t against t. Straight-line plots of t/q_t versus t were obtained for the adsorption of Zn^{2+} and Cu^{2+} (Figure 3). The calculated, k_2 and R^2 were determined from the graphs and are presented with the experimental in Table 1. The presence of linearity in the plots of t/q_t against t as well as the values of the coefficient of correlation, which were greater than 0.960, showed that the adsorption of Zn^{2+} and Cu^{2+} using plantain peel charcoal could best be described by the pseudo-second order kinetics. This is supported by the agreement of the calculated values with the experimental values. The intraparticle diffusion model which is given as

$$q_t = k_p t^{\frac{1}{2}} + I \tag{8}$$

where k_p and I are the intraparticle diffusion rate constant (mg.g^{-1}min$^{-1/2}$) and intercept (mg.g^{-1}) respectively.

Table 1: Kinetic Constants for Zn^{2+} and Cu^{2+} Adsorption on Plantain Peel Charcoal at Different Temperatures [(T (°C); (q_e) exp $(mg.g^{-1})$; (q_e) cal $(mg.g^{-1})$; k_1 (min^{-1}); k_2 $(g.mg^{-1}.min^{-1})$; kp $(mg.g^{-1}.min^{-1/2})$]

		Pseudo-first Order			Pseudo-second Order			Intraparticle Diffusion		
T	(q_e) exp.	(q_e) calc.	k_1	R^2	(q_e) calc.	k_2	R^2	I	kp	R^2
					Zn^{2+}					
10	4.9870	2.3261	0.0354	0.6673	5.2304	0.0243	0.9995	3.3429	0.1393	0.7142
20	5.3190	0.7408	0.0232	0.1779	5.2916	0.0927	0.9984	4.5873	0.0551	0.5931
30	5.6160	0.8169	0.0139	0.2242	5.6957	0.0567	0.9995	4.7379	0.0724	0.6715
40	6.0780	1.7522	0.0431	0.4010	6.3207	0.0262	0.9990	4.5546	0.1296	0.7583
50	6.0650	1.7673	-0.0309	0.3352	6.2779	0.0256	0.9993	4.5024	0.1296	0.8101
					Cu^{2+}					
10	3.8220	8.1060	0.0314	0.8949	-5.7120	0.0005	0.2069	-2.0825	0.4800	0.8628
20	4.6830	23.8764	0.0469	0.6702	-8.0418	0.0003	-0.0131	-1.5934	0.5062	0.9541
30	4.8080	9.9559	0.0373	0.5923	6.4470	0.0028	0.9897	0.4177	0.3577	0.9167
40	6.2550	46.6387	0.0614	0.7485	6.4078	0.0206	0.9976	4.3990	0.1435	0.8360
50	6.5580	2.7202	0.0550	0.8055	6.5928	0.1390	0.9999	6.3328	0.0171	0.8944
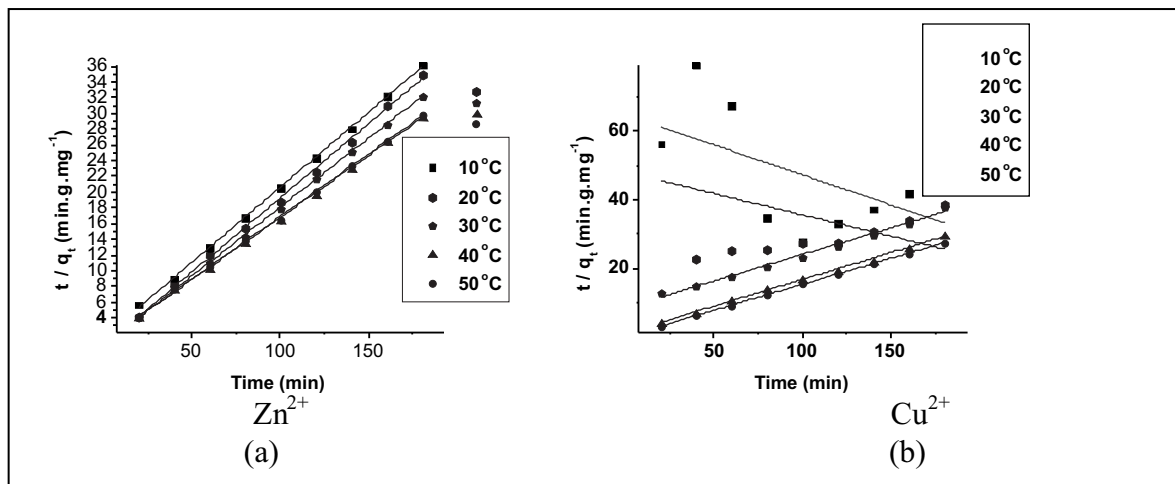
Figure 3: Pseudo-second Order Adsorption Kinetics of Zn^{2+} and Cu^{2+} Removal by Plantain Peel Charcoal.
(a) Pseudo-second Order Adsorption Kinetics of Zn^{2+} Removal by Plantain Peel Charcoal
(b) Pseudo-second Order Adsorption Kinetics of Cu^{2+} Removal by Plantain Peel Charcoal

The value of *I* indicates the degree of boundary layer, and the larger the value of I, the greater the boundary layer. A plot of the amount adsorbed against the square root of time should give a linear relationship if intraparticle diffusion is involved in the adsorption process and it is the rate controlling step if the line passes through the origin (Senthikumaar *et al.*, 2006). When the line does not pass through the origin, it indicates some degree of boundary layer control. By extension, it implies that intraparticle diffusion is not the only rate limiting step but other kinetic processes may control the rate of adsorption and all the processes may be operating simultaneously (Mahmoodi, 2011). From the values obtained (Table 1), the line did not pass through the origin. Hence intraparticle diffusion is not the rate controlling mechanism and it did not play any significant role in the uptake of Zn^{2+} and Cu^{2+} on plantain peel charcoal.

Adsorption Isotherms of Zn^{2+} and Cu^{2+} unto Plantain Peel Charcoal
An adsorption isotherm is a curve that relates the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the

liquid with which the adsorbent is in contact. Several equilibrium isotherms have been used in adsorption applications. In this work, Langmuir and Freundlich isotherms were applied to the adsorption data generated. The linearized form of the Langmuir equation (Langmuir, 1916) is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{Q_o} \qquad (9)$$

where q_e is the amount of heavy metal adsorbed on the adsorbent (mg.g^{-1}), C_e is the final concentration of metal (mg.L^{-1}) in the solution, Q_o is the maximum possible amount of metallic ion adsorbed per unit weight of adsorbent (mg.g^{-1}) and K_L is an equilibrium constant related to the affinity of the binding sites for the metals (L.mg^{-1}).

The Langmuir isotherm was used to test the experimental data for the removal of both metals using plantain peel charcoal, and the values of Q_o, K_L and R^2 were determined by plotting C_e/q_e

against C_e which gave linear plots as shown in Figures 4 (a, b, c, d, e) for Zn^{2+} and 5(a, b, c, d, e) for Cu^{2+}. The values of the correlation coefficient (R^2 greater than 0.970) are presented in Table 2. The linearity of the plots showed that the uptake of Zn^{2+} on the surface of plantain peel charcoal from synthetic wastewater can be described by the Langmuir isotherm at the different temperatures studied and at 40 and 50°C in the case of Cu^{2+}. The linearized form of the Freundlich equation is generally expressed as

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \qquad (10)$$

where q_e = heavy metal adsorbed on the adsorbent (mg.g^{-1}), C_e is the final concentration of metal (mg.L^{-1}) in the solution, k_F is a constant that provides an indication of the adsorption capacity of the adsorbent (L.g^{-1}), and $1/n$ is a constant that indicates the intensity of adsorption. Linear plots of q_e versus $\log C_e$ were obtained for the adsorption of Cu^{2+} and Zn^{2+} using plantain peel charcoal.
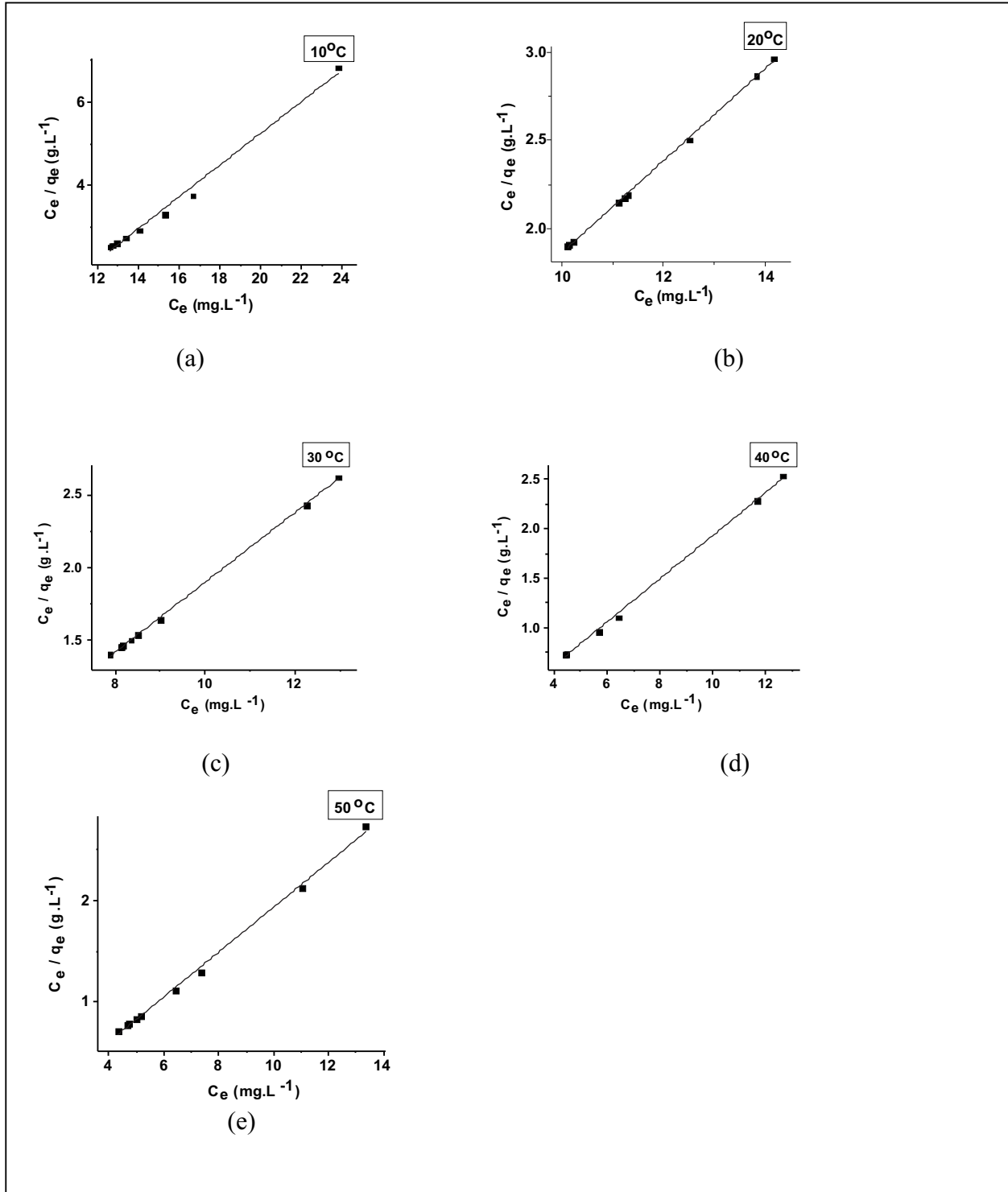
Figure 4: Langmuir Isotherms for Zn^{2+} Removal by Plantain Peel Charcoal
(a) Langmuir Isotherm of Zn^{2+} Removal by Plantain Peel Charcoal at 10°C
(b) Langmuir Isotherm of Zn^{2+} Removal by Plantain Peel Charcoal at 20°C
(c) Langmuir Isotherm of Zn^{2+} Removal by Plantain Peel Charcoal at 30°C
(d) Langmuir Isotherm of Zn^{2+} Removal by Plantain Peel Charcoal at 40°C
(e) Langmuir Isotherm of Zn^{2+} Removal by Plantain Peel Charcoal at 50°C
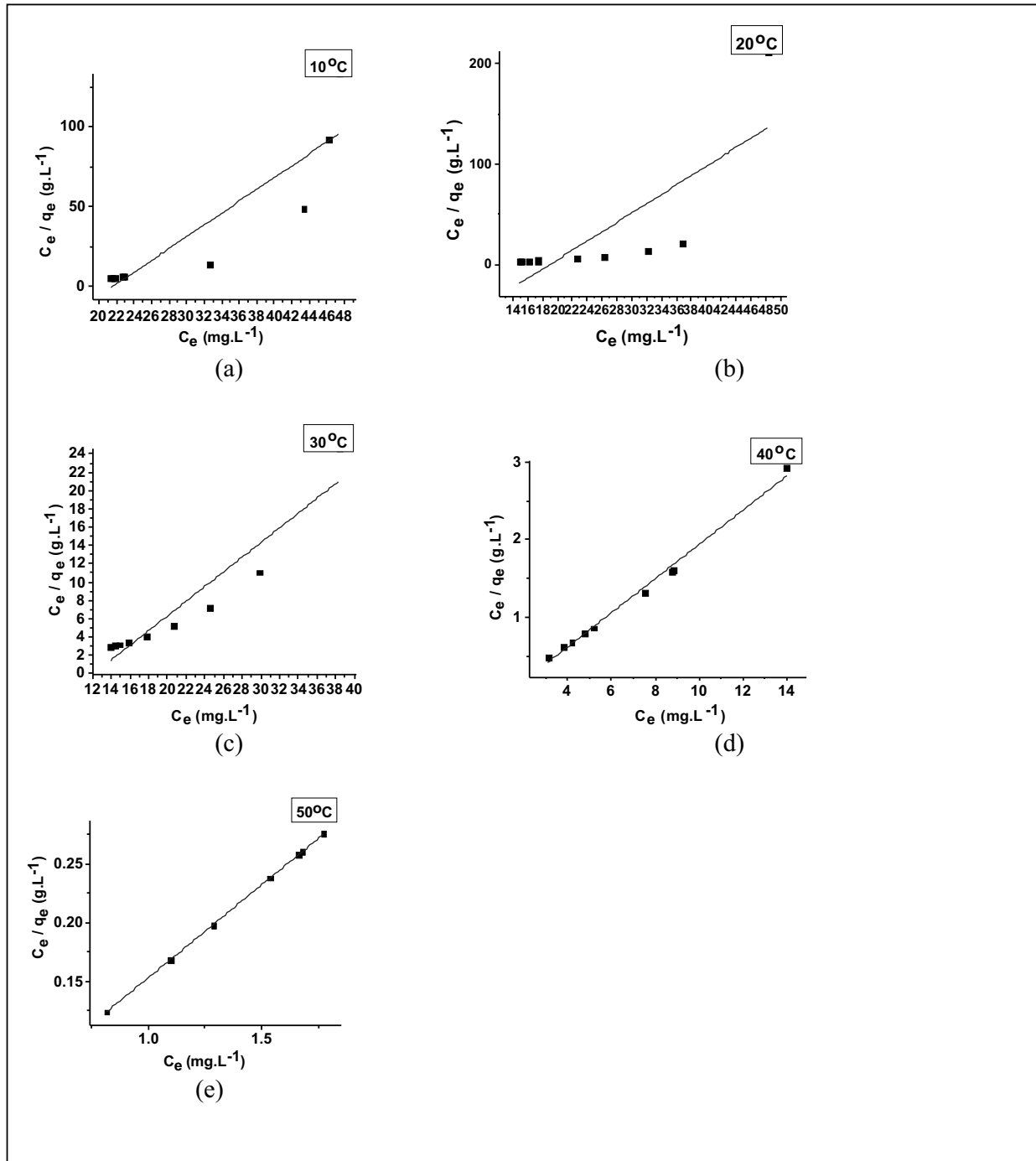
Figure 5: Langmuir Isotherms for Cu^{2+} Removal by Plantain Peel Charcoal
(a) Langmuir Isotherm of Cu^{2+} Removal by Plantain Peel Charcoal at 10°C
(b) Langmuir Isotherm of Cu^{2+} Removal by Plantain Peel Charcoal at 20°C
(c) Langmuir Isotherm of Cu^{2+} Removal by Plantain Peel Charcoal at 30°C
(d) Langmuir Isotherm of Cu^{2+} Removal by Plantain Peel Charcoal at 40°C
(e) Langmuir Isotherm of Cu^{2+} Removal by Plantain Peel Charcoal at 50°C

Table 2. Isothermal Constants for Zn^{2+} and Cu^{2+} Adsorption on Plantain Peel Charcoal at Different Temperatures $[(Q_0 \ (mg.g^{-1}); K_L \ (L.mg^{-1}); K_F \ (L.g^{-1})]$

	Zn²⁺					
	Langmuir				Freundlich	
T	K$_L$	Q$_0$	.	K$_F$	1/n	R²
10	-0.1614	2.6305	0.9911	20.2628	-0.5488	0.9795
20	-0.3463	3.8216	0.9991	11.0729	-0.3160	0.9958
30	-0.4807	4.1641	0.9996	9.6095	-0.2587	0.9973
40	-0.8689	4.5788	0.9987	8.0330	-0.1843	0.9834
50	-0.7809	4.5065	0.9970	8.1686	-0.1911	0.9725
	Cu²⁺					
10	-0.0464	0.2705	0.7889	12753.5180	-2.6145	0.9185
20	-0.0528	0.2149	0.5703	1121.4760	-1.9282	0.6921
30	-0.0701	0.8164	0.8392	72.6524	-0.9997	0.9043
40	-0.8663	4.5633	0.9920	7.7446	-0.1656	0.9236
50	-34.3987	6.3335	1.0000	6.5278	-0.0246	0.9906

The values of k_F, 1/n and R^2 were determined and are given in Table 2. The R^2 values and linear fit between log q_e versus log C_e showed that the adsorption of Zn^{2+} and Cu^{2+} using plantain peel charcoal can be approximated with the Freundlich model as well. However, the best fit was obtained using the Langmuir model. Hence plantain peel charcoal is a good adsorbent for the removal of Cu^{2+} and a better adsorbent for Zn^{2+} from synthetic wastewater.

Adsorption Thermodynamics of Zn^{2+} and Cu^{2+} onto Plantain Peel Charcoal

Thermodynamic parameters such as changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were also investigated. From the values of these parameters, the spontaneity of the adsorption process can readily be determined. Whether the process is endothermic or exothermic in nature along with the degree of disorderliness can also be determined. These parameters were determined from the following equations (Mahmoodi, 2011; Ozcan *et al.*, 2006):

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

$$K_C = \frac{C_A}{C_S} \tag{12}$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ \text{(Van't Hoff Equation)} \tag{13}$$

where K_C is the equilibrium constant, C_A is the amount of solute adsorbed and C_S is the equilibrium concentration of the solute in the solution.

The Van't Hoff Equation was used by plotting ln K_c versus 1/T. The values of ΔS and ΔH were calculated from the intercept and slope respectively. ΔH was found to be positive at the different temperatures (Table 3), which implied that the adsorption process was endothermic in nature.

Table 3: Thermodynamic Parameters for Zn^{2+} and Cu^{2+} Adsorption on Plantain Peel Charcoal [T (K); ΔS (kJ mol^{-1}.K^{-1}); ΔH (kJ.mol^{-1}); and ΔG (kJ.mol^{-1})]

Metals	ΔS (J.mol^{-1}.K^{-1})	ΔH (kJ.mol^{-1})	ΔG(kJ.mol^{-1})				
			283K	293K	303K	313K	323K
Zn^{2+}	0.1004	25.9279	-2.4738	-3.4774	-4.4810	-5.4845	-6.4881
Cu^{2+}	0.2499	71.0734	0.3463	-2.1529	-4.6521	-7.1513	-9.6505

This was confirmed by the increase in the adsorption capacity with the rise in temperature. The positive values of ΔS suggested that randomness increased on the solid - solution interface during the adsorption process. The negative values of ΔG implied that the adsorption process was spontaneous. The reduced values of ΔG as the temperature increased indicated that the process was more spontaneous at higher temperatures (Mahmoodi, 2011). For physisorption reaction, free energy change is generally between -20 to 0 kJ.mol^{-1}, while it is between -80 to -400 kJ.mol^{-1} for chemisorption reaction (Jaycock and Parfitt, 1981). From the results of this study, the ΔG values calculated fell within the range -20 to 0 kJ.mol^{-1} implying that the adsorption process involved a physisorption reaction. This meant that chemical bonds were not formed between the ions and the adsorbent surface. Hence, subjecting the used charcoal to mild desorption and reactivation procedures would enhance its recycling and further usability.

CONCLUSIONS

The kinetics, thermodynamics and equilibrium study of Zn^{2+} and Cu^{2+} adsorption from wastewater showed that the adsorption process was a physisorption, endothermic and spontaneous reaction implying that desorption process and reuse of plantain peel charcoal for water recycling purposes will be readily achievable. Its high removal efficiency combined with the insight gained into the mechanism by which plantain peel charcoal adsorbs heavy metal species such as Zn^{2+} and Cu^{2+} from wastewaters could be harnessed in its applications as a viable low cost alternative to the existing hi-tech adsorption procedures especially in the developing countries.

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