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Kinetic Studies on the Sorption of Ag^+ and Al^{3+} from Aqueous Solutions by Coconut Fibre

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ABSTRACT

Kinetic investigations are necessary for determining the rate of a reaction and the mechanism. The kinetics of sorption of Ag+ and Al^{3+} ions from aqueous solution onto coconut fibre biomass under different experimental conditions was investigated in this study. The influence of initial Ag^+ and Al^{3+} ions, pH (1 to 11), temperature (273 to 373 K), and time (10 to 120 min), at a constant concentration of metal ions (100 mg/L) is reported. The amount of metal ions adsorbed increased slightly as time increased. Al^{3+} was adsorbed more than Ag^+. Adsorption of the Ag^+ ion was more highly pH-dependent and the optimum pH for removal was ~7.0. The adsorption of Al^{3+} was more time-dependent and the optimum time for removal was 120 min. A comparison of kinetic models applied to the sorption process was evaluated for the pseudo first-order, pseudo second-order and Ritchie's second-order kinetic models, with the pseudo second-order giving a better fit to the experimental data. From the results of the temperature effect, the thermodynamic constants ΔG^O; ΔH^O, E_A and ΔS^O for the sorption process were evaluated. The values obtained for ΔG^O were all negative while those obtained for $E_{A,}$ ΔS^O and ΔH^O were positive. The data showed that the sorption process was feasible, spontaneous and endothermic in nature. The sticking probability model was further employed to assess the applicability of coconut fibre as an alternative adsorbent for Ag^+ and Al^{3+} contaminants in an aqueous system. The findings of this investigation suggests that physical sorption plays a significant role in controlling the sorption rate and that coconut fibre is an excellent adsorbent for Ag^+ and Al^{3+} ions removal from aqueous solution.

Keywords: adsorption, aqueous solution, environment, heavy metal, kinetics

INTRODUCTION

Environmental pollution problems caused by heavy metals (HMs) cannot be over emphasized. HMs are very toxic and pose a threat to man and the environment. The amount of these HMs in our environment increases as a result of industrialization. The anthropogenic sources of HMs include waste from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, and leachates from landfills and contaminated ground water from hazardous waste sites (Reed *et al*. 1994).

Recent developments in environmental quality standard highlight the need for improved wastewater treatment of dilute metal-bearing effluents (Ho and McKay 1999). A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverses osmosis, chemical precipitation and adsorption (Qadeer and Akhtar 2005). As a result of the expensive nature, economically non-feasibility for small scale industries, drawbacks such as high capital and operational costs or the disposal of the residual metal sludge, for the conventional methods mentioned above, it is therefore necessary to search for alternative sorbents which are inexpensive, often naturally occurring, biodegradable materials that have good sorbent properties and low value to the inhabitants.

Sorption has been described as an effective separation process for a wide variety of applications, while kinetics describes the solute uptake rate that controls the residence time of sorbate uptake at the solid-solution interface. Kinetics is so important that it can be used to predict the rate of pollutant removal from aqueous solutions in the design of appropriate sorption treatment plants (Ho and McKay 1999). It is therefore understandable that the study of sorption kinetics in wastewater treatment is significant as it provides valuable insight into the reaction pathways and into the mechanism of sorption reactions. (Ho and McKay 1999)

Many researches have reported the development of low-cost adsorbents from cheaper and readily available materials (Pollar *et al*. 1992; Bailey *et al*. 1999; Babel and Kurniawnata 2003). The adsorption of metal ions by a number of materials such as leaf mould (Sharma and Forster 1994), activated groundnut husk carbon (Srinicason *et al*. 1991) coconut husk (Igwe and Abia 2006; Igwe *et al*. 2008), coconut shell activated carbon (Alaerts *et al*. 1989), cassava waste (Abia *et al*. 2003), coconut shell, wood and dust coal activated carbon (Selomulya *et al*. 1999), lichen (*Cladonia furcata*) biomass (Sari *et al*. 2007), boiler fly ash (Okoronkwo *et al*. 2008), waste acorn of *Quercus ithaburensis* (Malkoc and Nuhoglu 2007), acid washed crab shells (Niu and Volesky 2007), maize cob and husk (Igwe and Abia 2003, 2005, 2007), mimosa tannin resin (Turkmenler *et al*. 2008), pumpkin seed husk (Ikhuoria and Omonmhenle 2006), and so on, have been reported. In this work, coconut fibre an agricultural waste was used to remove Al^{3+} and Ag^+ ions from aqueous solution. Adsorption studies were carried out using time, pH and temperature as reaction parameters at constant initial metal ion solution concentration.

MATERIALS AND METHODS

Materials

The coconut (*Cocos nucifera*) fruit used was obtained from a local market in Okigwe, Imo State Nigeria and was properly identified in the Department of Plant Science and Biotechnology, Abia State

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University, Uturu Nigeria. The fibrous part was extracted, washed, air-dried and ground to smaller particles. The ground fibre was then sieved and the particle size of 250-300 µm was used for the experiment. This particle size was soaked in 2% (v/v) dilute nitric acid (HNO_3) solution for 24 hrs. All reagents used were of good analytical grades used as purchased with out further purifications.

Methods

1. Adsorbent characterization

The surface characteristics of the coconut fibre were determined (Santamarina *et al*. 2002). Parameters such as specific surface area (S_{AA}), Specific charge density (SCD), pore size, pore volume, porosity, bulk density, particle density and cation exchange capacity (CEC) were determine. Stock solutions of Ag^+ and Al^{3+} metal ions of 100 mg/L concentrations were prepared by dissolving known amounts of silver nitrate ($AgNO_3$) and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_20$) respectively in 1 L of deionized water. Various aliquots of the working solutions were then collected from these stock solutions.

2. Sorption of metal ions on coconut fibre

Effect of time: 100 mL of the stock solution of the metal ions in the volumetric flask were transferred into 250 mL conical flasks containing 1 g each of the adsorbent. The flasks were corked and agitated for a given time interval of 10, 20, 30, 40, 50, 60 and 120 min. At the end of each time, the flasks were filtered rapidly and the filtrate was collected for Atomic Adsorption Spectroscopy analyses using Atomic Adsorption Spectrophotometer (AAS), UNICAM 919 model.

Effect of pH: 100 mL of the standard solution of the metal ions was collected in 250 mL conical flasks and their pH was adjusted to 1, 3, 7, 9 and 11 for both Ag^+ and Al^{3+} ions solutions using dilute sodium hydroxide (0.1 M NaOH) and dilute hydrochloric acid (0.1 M HCl). 1 g each of the adsorbent was then added to the metal ions solutions having the above mentioned pH range. The flasks were agitated for 1 h in a constant temperature rotary shaker. After 1 h, the flasks were filtered, the final pH of the solution was recorded and the metal content of the filtrate was analyzed using Atomic Adsorption Spectrophotometer (AAS), UNICAM 919 model.

Effect of temperature: 100 mL of the standard solution of the metal ions were collected in 250 mL conical flasks and 1 g each of the adsorbent was added. Different solutions were agitated for 1 h at different temperatures: 273, 303 and 373 K. At the end of 1 h, the metal content of the filtrate was analyzed as stated above.

All experimental readings were performed in triplicate and the average of each reading was used in the calculations.

RESULTS AND DISCUSSION

The activation of the adsorbent by 2% (v/v) nitric acid served to open-up the pores in readiness for adsorption process. It also served to dissolve any soluble biomolecule and wash off debris from the surface of the adsorbent, which might interfere with sorption process. The surface characteristics of the coconut fibre are reported on **Table 1**. The specific surface area (S_{AA}) and specific charge density (SCD) are very high depicting probability for high metal sorption.

The mean amount of metal adsorbed by the adsorbent was determined using a mass balance equation expressed as;

$$q_t = (C_e - C_o)\ V/m \qquad (1)$$

where q_t is the metal ion adsorbed at any given time t (mg/g); C_e is the metal ion concentration in solution (mg/L) at equilibrium; C_o is the initial metal ion concentration in solution (mg/L); V is the volume of initial metal ion solution used (mL) which is constant (100 mL); m is the mass of adsorbent used (1 g).

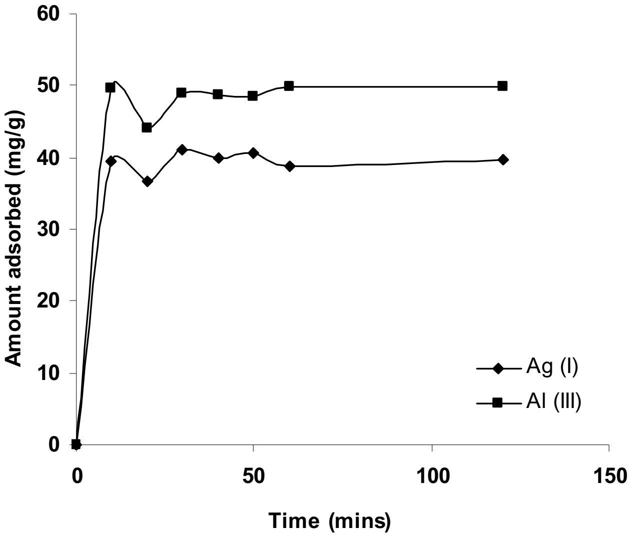

Fig. 1 Amount adsorbed (mg/g) against contact time (mins) for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

Effect of contact time

The experimental results for the amount of Ag^+ and Al^{3+} adsorbed as time increased are shown on **Fig. 1**. The amounts of the metal ions adsorbed increased slightly as time was increased. The amount of Al^{3+} adsorbed was higher than that of Ag^+. This could be explained based on the ionic radii of the metal ions. The ionic radius of Ag^+ is 129.0 ρm while that of Al^{3+} is 69.0 ρm. It has been reported that the smaller the ionic diameter the higher the adsorption rate (Uzun and Guzel 2000). Therefore, from our studies, Al^{3+} with smaller ionic radius has higher adsorption rate more than Ag^+ with higher ionic radius. The sorption trend could also be explained based on the trend of hydration energies of the metal ions (ΔH_{hyd}). This is given as –4660 KJ/mol for Al^{3+} and –475 KJ/mol for Ag^+ ion (Burgess 1978). Again, the trend of hydration energies confirms the trend of sorption of the metal ions on coconut fibre. Let the hydrolysis reaction of the metal ions be represented by the equation below:

$$M^{n+} + nH_2O \leftrightarrow M\ (OH)\ n + nH^+ \qquad (2)$$

Equation (2) above essentially takes place in two steps, which may be given as:

$$M^{n+} + (n\text{-}1)\ H_20 \leftrightarrow MOH^{\ (n\text{-}1)+} + H^{(n\text{-}1)+} \qquad (3)$$

$$MOH^{\ (n\text{-}1)+} + (n\text{-}1)\ H_20 \quad \leftrightarrow \quad M\ (OH)n + H^{(n\text{-}1)+} \qquad (4)$$

where n is 1 for Ag and 3 for Al.

This means that in aqueous solution before adsorption

Table 1 Surface characteristics of unmodified and activated coconut fibre.

Parameter	Value (unit)	Parameter	Value (unit)
Bulk density	0.062 (g/cm^3)	Specific surface area (S_{AA})	1.186 × 10^{25} (m^2/g)
Particle density	0.256 (g/cm^3)	Surface charge density (SCD)	5.39 × 10^{24} (meq/m^2)
Pore volume	3.9 (cm^3/g)	Particle size	250-500 µm
Cation exchange capacity (CEC)	64.0 (mg/100 g)	pH	5.35
Porosity	18.14 (%)	Colour	Brownish

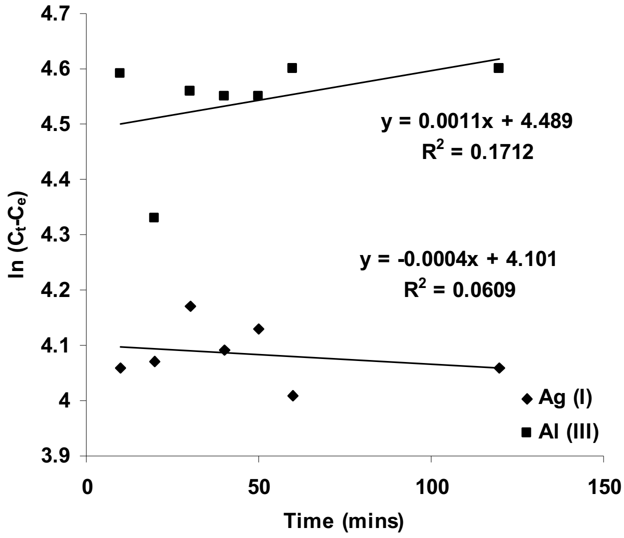

Fig. 2 Pseudo first order plot for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

takes place, these reactions will occur. Therefore, the HM that becomes more hydrolyzed will be the least adsorbed. Going by the hydration enthalpies of the metal ions given above, we expect and rightly too, that Ag^+ will be hydrolyzed more than Al^{3+}, hence Al^{3+} was the more adsorbed.

Sorption kinetics

The experimental results were modeled using three kinetic equations which included; pseudo-first order, pseudo-second order and Ritchie's second order equations. The pseudo first-order equation as developed by Lo and co-workers and reported by Qadeer and Akhtar (2005) was used. This equation is expressed as

$$C_t - C_e = D \exp (K_1 t) \qquad (5)$$

where C_t is the metal ion concentration adsorbed at time t (mg/g), C_e is the metal ion concentration at equilibrium (mg/L), t is the contact time (mins), D is a fitting parameter and K_1 is a constant. Equation (5) could be linearized as follows;

$$\text{In}\,(C_t - C_e) = \text{In}\, D + K_1 t \qquad (6)$$

The plot of ln (C_t-C_e) against t is shown in **Fig. 2**. The Linear regression equations and the coefficient of determination (R^2) are shown on the same figure.

The pseudo second-order model is given as (Ho *et al.* 2000);

$$dq_t/d_t = K_2\,(q_e - q_t)^2 \qquad (7)$$

where K_2 is the rate constant of pseudo-second order adsorption (g/mg-min). Integrating equation (7) and applying the boundary conditions t = 0 to t = t and q_t = 0 to qt = qt, will give;

$$1/(qe - q_t) = 1/qe + K_t \qquad (8)$$

Equation (8) is the integrated rate law for pseudo-second order reaction. Rearranging gives a linear form as:

$$t/qt = 1/K_2 qe^2 + t/qe \qquad (9)$$

If the initial adsorption rate, h_o (mg/g-min) is

$$h_o = K_2 qe^2 \qquad (10)$$

Then equations (9) and (10) becomes

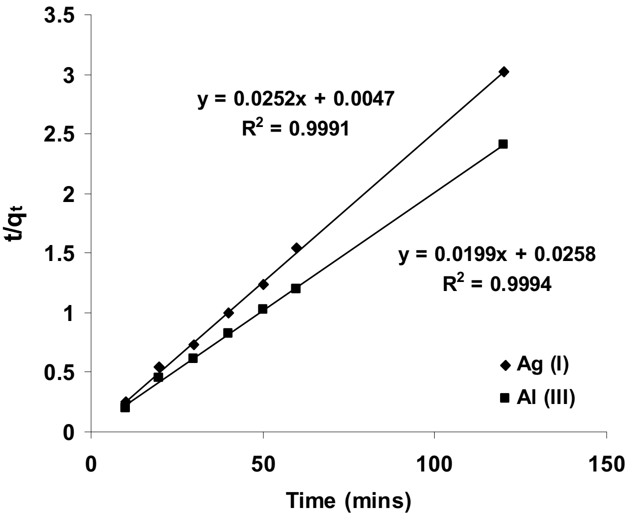

Fig. 3 Pseudo second order plot for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

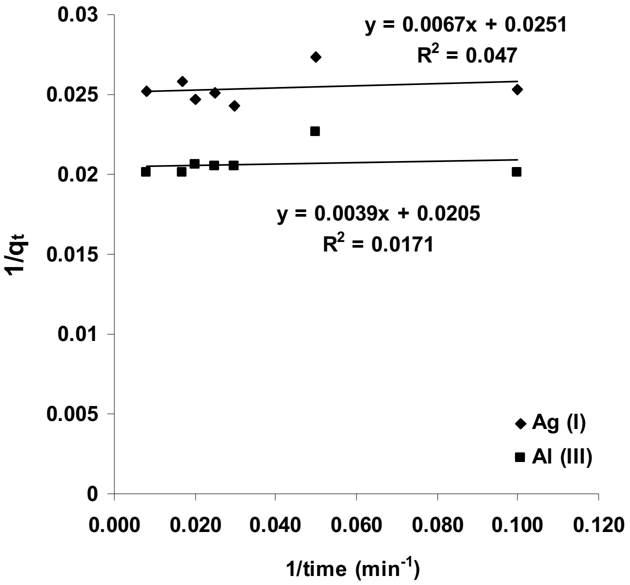

Fig. 4 Ritchie's second order plot for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

$$t/q_t = 1/h_o + t/q_e \qquad (11)$$

The plots of t/qt against t for the metal ions are shown in **Fig. 3**. The linear regression equations and the coefficient of determination (R^2) are shown on the same figure.

Another kinetic model used, the Ritchie's second-order equation is given as (Ritchie 1977):

$$1/q_t = 1/\,(Kq_e\, t) + 1/q_e \qquad (12)$$

where K is the rate constant (min^{-1}) of the second order adsorption. The plots of 1/qt against 1/t for Ag^+ and Al^{3+} adsorption on coconut fibre are shown in **Fig. 4**. The linear regression equations and the coefficient of determination (R^2) are shown on the same figure.

From the respective plots of the three kinetic models, the rate constants and other constants for the equations were evaluated from the slopes and intercepts of the plots. These constants and R^2 values are shown on **Table 2**. It could be observed that the pseudo-second order model gave a better fit to the experimental data as seen from the high values of R^2 given as 0.9994 for Al^{3+} and 0.9991 for Ag^+ ion. The Ritchie's second-order model and the pseudo first-order model gave very poor correlations for both metal ions. Therefore,

Table 2 Rate constants and R^2 values for kinetic models of Ag (I) and Al (III) adsorption on coconut fibre.

Metal ions	Pseudo-first order			Pseudo-second order				Ritchie's second order		
	K	ln D	R^2	h_o	K_2	qe	R^2	K_2	qe	R^2
Ag^+	$1.0x10^{-4}$	4.101	0.0609	212.77	0.135	39.68	0.9994	3.746	39.84	0.0470
Al^{3+}	$1.1x10^{-3}$	4.489	0.1712	38.76	0.015	50.25	0.9991	5.257	48.78	0.0171

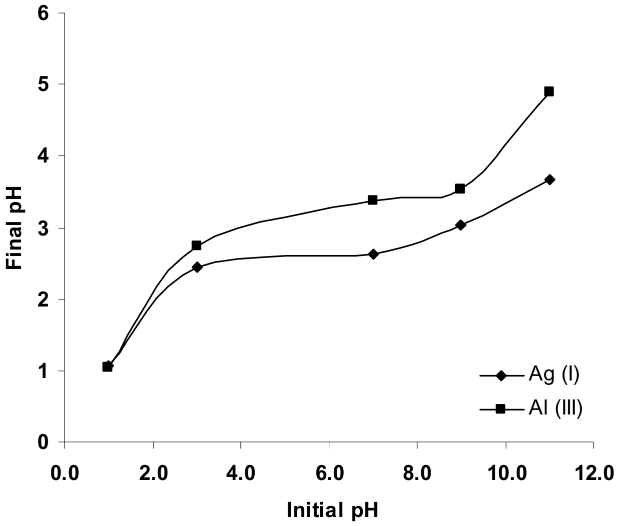

Fig. 5 Initial pH against final pH of effluent for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

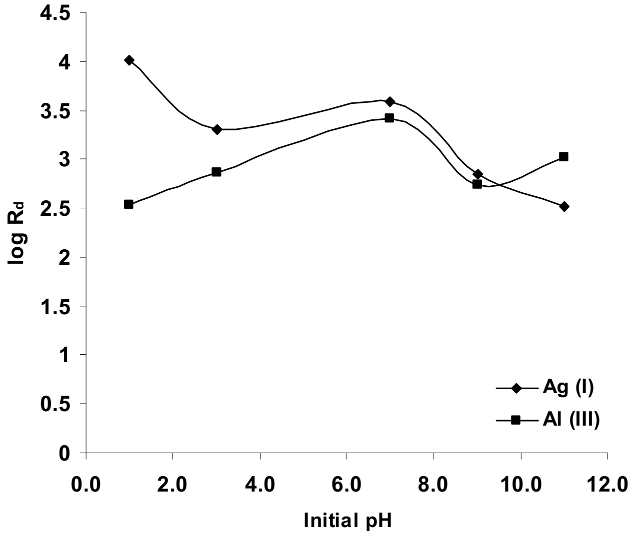

Fig. 7 Distribution coefficient for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

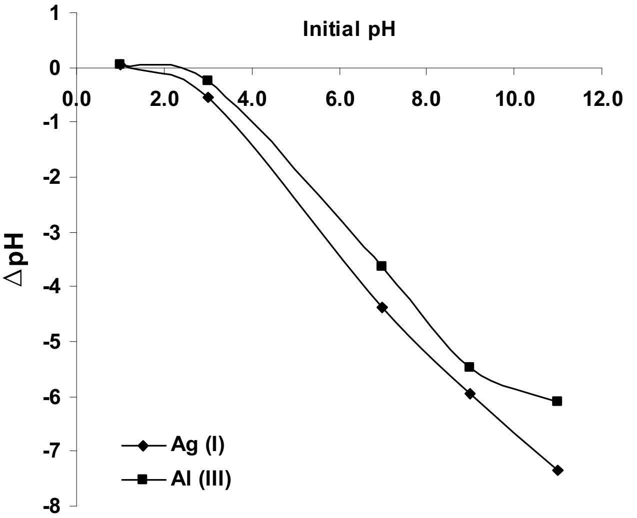

Fig. 6 ΔpH against initial pH for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

the sorption experimental data for adsorption of Al (III) and Ag (I) ions on coconut fiber fits the pseudo second order model.

Effect of pH

Fig. 5 shows the plot of final pH of metal ion solution after adsorption reaction against initial pH of metal ions solution before adsorption. It could be seen that as the initial pH of the metal ion solution was increased, the final pH also increased with that of Al^{3+} being higher than Ag^+. The increase in the final pH depicts that there was displacement of H^+ ions by the metal ions as in ion exchange as the sorption reaction takes place. The pH at zero point of charge (pH_{zpc}) was evaluated by calculating ΔpH (difference between initial and final pH) and plotting it against initial pH (**Fig. 6**). The values of pH_{zpc} can be determined from the curve that cuts the initial pH line of the plot of ΔpH against initial pH. From this study, the pH_{zpc} for the coconut fibre used for the sorption is pH 1.1. The pH_{zpc} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution. Cations adsorption will be more favorable at pH value higher than pH_{zpc}. Hence, the optimum pH for the sorption process was found to be 7.0 which is higher than the pH_{zpc}.

Fig. 7 shows the plot of log R_d (distribution coefficient) against pH of metal ion solution as shown by equation (13).

$$R_d = (V/m)\ (C_t/C_o\text{-}C_t) \qquad (13)$$

where R_d is the distribution coefficient; V is the volume in mL; m is the mass of adsorbent (g); C_t is amount adsorbed (mg/g) at time t (mins); Co is the initial concentration of metal ion solution (mg/L). From **Fig. 7**, it could be observed that increasing the solution pH decreases the amount of Al^{3+} adsorbed from pH 1 to about pH 3, increases again up to pH 7, decreases again up to pH of 9 and then increases slightly up to pH of 11. The optimum pH for the adsorption of Al 3+ was found to be pH 7.0. For Ag+ the amount adsorbed increased from pH 1 to pH 3, decreases up to pH 9 and increased again up to pH of 11. The optimum pH being about 7.0. The increase in amount adsorbed with pH is attributed to the fact that decreasing solution pH increases H^+ concentration in solution which co-ordinates with-OH groups to form $-OH_2^+$ and will reduce the number of negative sites on the adsorbent and cause repulsion of Ag^+ and Al^{3+} ions (Ofomaja *et al.* 2005). On the other hand, increasing pH reduces the amount of H^+ in solution and promotes ionization of -OH groups, thus increasing cation exchange capacity.

Effect of temperature

Temperature is one of the crucial parameters in adsorption reactions. The result of the variation of temperature on sorption capacity is shown on **Fig. 8** as amount adsorbed (mg/g) against temperature (K). The amount adsorbed increased as temperature increased from 273K to 373K. This trend is similar to previous reports (McKay *et al.* 1999; Ho 2003). The amount of Al^{3+} adsorbed was higher than that of Ag+ at

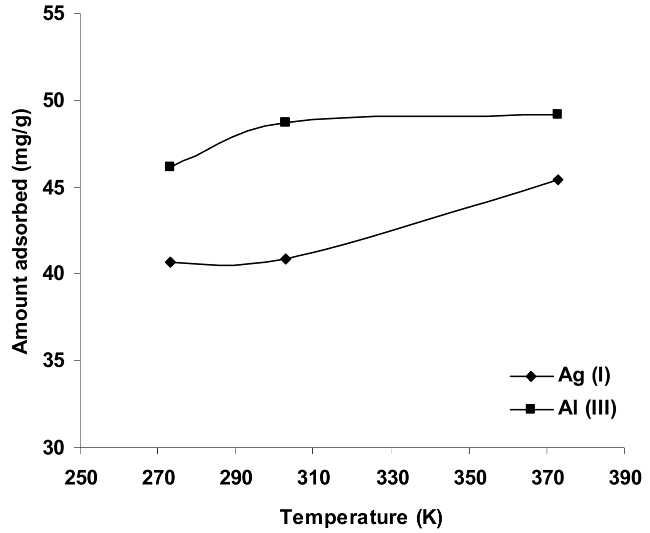

Fig. 8 Amount adsorbed (mg/g) against temperature (K) for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

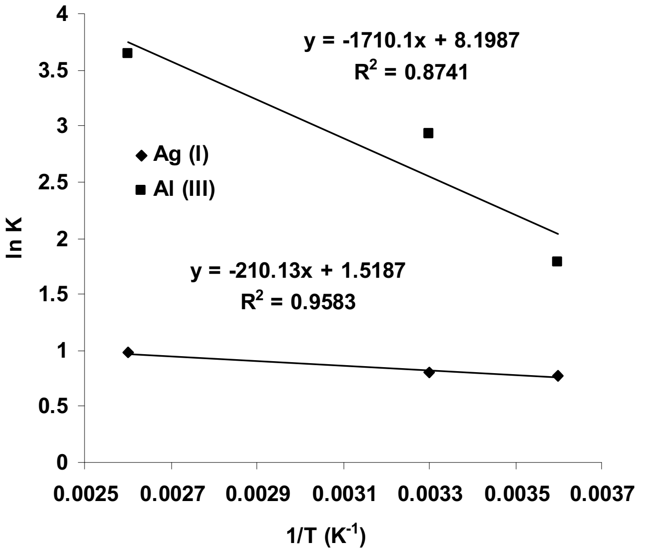

Fig. 9 Vant Hoff plot for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

all temperatures tested. A process can give out heat to the surroundings or take up heat from its surroundings; this is called exothermic and endothermic reactions respectively. When a reaction is endothermic, the increase in temperature favours the reaction. On the other hand when a process is exothermic, increase in temperature does not favour the reaction in adsorption process. This is because the thickness of the boundary layer decreases due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase which results in a decrease in adsorption as temperature increases (Aksu and Kutsal 1991). From the results of this study, it means that the sorption process is endothermic. Temperature has been used to classify adsorption reactions as either chemisorptions or physisorption processes. A decrease in adsorption with increasing temperature suggests weak adsorption interaction between biomass surface and the metal ion, which suggests physisorption.

Thermodynamic treatment of sorption process

To determine the spontaneity of a process in engineering practice, values of thermodynamic parameters such as enthalpy change (ΔH^O), entropy change (ΔS^O), activation energy (E_A) and Gibbs free energy change (ΔG^O) must be taken into consideration. The thermodynamic parameters were evaluated from the following equations.

$$K = C_{Ad}/Ce \tag{14}$$

$$\ln K = \Delta S^O/R - \Delta H^O/RT \tag{15}$$

$$\Delta G^O = -RT \ln K \tag{16}$$

where K is the equilibrium constant, C_{Ad} is the amount of metal ion adsorbed (mg/g), Ce is the equilibrium solution phase concentration of metal ion, R is universal gas constant (8.314 JK^{-1} mol^{-1}), ΔH^O (KJ mol^{-1}) is the enthalpy change, ΔS^O (JK^{-1} mol^{-1}) is the entropy change, E_A (KJ mol^{-1}) is the activation energy and ΔG^O (KJmol^{-1}) is the Gibbs free energy change. The plot of InK versus 1/T (Vant Hoff) for the metal ions is shown on **Fig. 9**. The regression equations and R^2 values are also shown. From the linear regression equation, the values of ΔS^O and ΔH^O were calculated from the intercepts and slopes of the plots. Then, using Equation (16), the values of ΔG^O were calculated at different temperatures. The values obtained for the thermodynamic parameters are shown on **Table 3**. The negative values of ΔG^O shows that the sorption process was spontaneous. A decrease in the value of ΔG^O as temperature increases depicts spontaneity. From our results, ΔG^O increases with temperature, this means that spontaneity also decreases with increasing temperature. This was confirmed by the positive value obtained for ΔH^O, showing that the process is endothermic. Therefore this corresponds to the increase in amount adsorbed as temperature was increased. Also, the values of ΔS^O obtained were positive and that of Al^{3+} was higher than that of Ag^+. Entropy change (ΔS^o) is a measure of the degree of disorderliness. Hence, this confirms that sorption capacity of Al^{3+} was higher than that of Ag^+. The sorption process can also be said to follow a physisorption mechanism because the value of ΔH^o falls within that range (Alkan *et al.* 2004).

The sticking probability model was used to ascertain whether the sorption process was of physisorption or chemisorption mechanism. It was also used to ascertain the probability of the metal ion remaining on the surface of the adsorbent. The potential sticking probability equation is given by:

$$S^* = (1-\Theta) \exp - (E_A/RT) \tag{17}$$

where Θ is known as the surface coverage and is given by:

$$\Theta = (1-Ce/Co) \tag{18}$$

where Co and Ce are the initial and equilibrium metal ion concentrations respectively. The plot of sticking probability is shown on **Fig. 10**. The values of S* evaluated at different temperatures are shown in **Table 3**. The guidelines for the

Table 3 Thermodynamic parameters of Ag (I) and Al (III) adsorption by coconut fibre.

Metal ions	Temp (K)	ΔG^O (KJ mol^{-1})	ΔS^O (JK^{-1} mol^{-1})	ΔH^O (KJ mol^{-1})	E_A (KJ mol^{-1})	S*
Ag^+	273	-1.77	12.62	1.747	13.72	0.280
	303	-2.02				0.300
	373	-3.04				0.320
Al^{3+}	273	-4.04	68.16	14.218	0.75	0.001
	303	-7.38				0.002
	373	-11.29				0.005

Table 4 The potential sticking probability relationship between sorbate and sorbent.

Values of S	Potential sticking probability
S*>1	Adsorbate unsticking to adsorbent-no sorption.
S*=1	Linear sticking relationship between adsorbate and adsorbent-possible mixture of physisorption and chemisorptions.
S*=0	Indefinite sticking of adsorbate to adsorbent chemisorption mechanism predominant.
0<S*<1	Favorable sticking of adsorbate to adsorbent physisorption mechanism predominant.

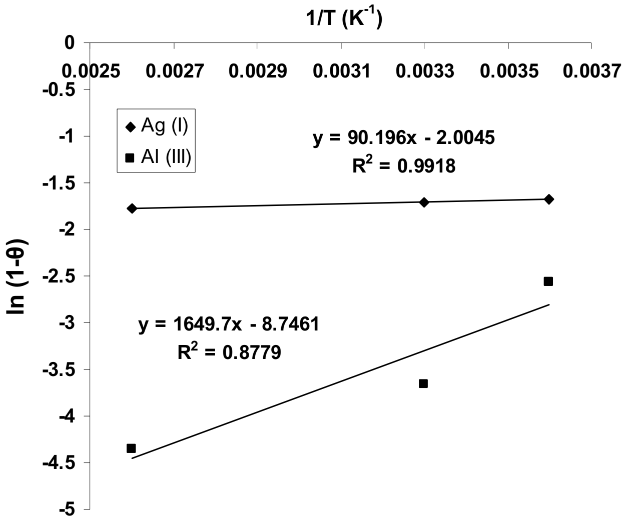

Fig. 10 Sticking probability plot for adsorption of Ag (I) and Al (III) ions from aqueous solutions using coconut fibre.

potential sticking probability relationships are shown in **Table 4**. From the values of S* in **Table 3** and the guidelines in **Table 4**, it could be seen that our system falls within category number 4. This means that there was favorable sticking of adsorbate to adsorbent and that physisorption mechanism predominates. Also, the values obtained for the sticking probability were higher for Ag^+ than for Al^{3+} ion.

CONCLUSION

The influence of agitation time, pH and temperature on the kinetics of Ag^+ and Al^{3+} removal from aqueous solution using coconut fibre was investigated and reported. The amount of the metal ions adsorbed was influenced by agitation time, pH and temperature. Al (III) ion was adsorbed more than Ag (I) ion. Amongst the three kinetic equations tested, the pseudo second-order model gave very good fit to the sorption process. The thermodynamic parameters were evaluated and their significance to reaction conditions was enumerated. The sticking probability model was used to confirm that physisorption was the predominant mechanism of the sorption process. Therefore, coconut fibre has been shown to be a good adsorbent for removal of Ag^+ and Al^{3+} from aqueous solution.

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