Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (Wild Cocoyam) biomass

Michael Horsfall Jnr*
Department of Pure and Industrial Chemistry
University of Port Harcourt
Uniport P.O.Box 402, Choba
Port Harcourt, Nigeria
Tel: 234 803 507 9595
E-mail: horsfalljnr@yahoo.com

Ayebaemi I. Spiff
Department of Pure and Industrial Chemistry
University of Port Harcourt
Uniport P.O.Box 402, Choba
Port Harcourt, Nigeria
Tel: 234 803 309 5183
E-mail: emispiff@yahoo.com

This report is based on the investigation of the effect of temperature on the removal of Pb^{2+} and Cd^{2+} in aqueous effluent using *C. bicolor* biomass in a batch sorption process. The result showed that the most suitable sorption temperature was 40ºC with maximum sorption capacities of 49.02 mg/g and 52.63 mg/g for Pb^{2+} and Cd^{2+} respectively. Various thermodynamic parameters, such as ΔG^o, ΔH^o, ΔS^o and E_a have been calculated. The data showed that the sorption process is spontaneous and exothermic in nature and that lower solution temperatures favours metal ion removal by the biomass. The findings of this investigation suggest that physical sorption plays a role in controlling the sorption rate. The sticking probability model was further employed to assess the applicability of the *C. bicolor* biomass as an alternative adsorbent for metal ion contaminants in aqueous system.

Temperature is a crucial parameter in adsorption reactions. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperatures. But for activated carbon, a different trend is noticed where decreasing viscosity and increasing molecular motion at higher temperature allows the uptake of molecules into the pores more easily, causing adsorption to increase as temperature increases. However, temperature has not been studied as relevant variable in biosorption experiments. The tests are usually performed at approximately 25-30ºC. However, Tsezos and Volesky, (1987); Kuyucak and Volesky (1989) and Aksu and Kutsal

(1991) reported a slight increase in cation uptake by seaweed in the range of 4 to 55ºC.

Heavy metals in the environment have become a major threat to plant, animal and human life due to their bioaccumulating tendency and toxicity and therefore must be removed from municipal and industrial effluents before discharge. It is therefore necessary that there are technologies for controlling the concentrations of these metals in aqueous discharges/effluents. The conventional technologies, which have been used, ranged from granular activated carbon to reverse osmosis (Gardea-Torresdey et al. 1998). However, these processes are not economically feasible for small-scale industries prevalent in developing economies due to huge capital investment. It is therefore necessary to search for alternative adsorbents, which are low-cost, often naturally occurring biodegradable products that have good adsorbent properties and low value to the inhabitants.

A range of products has been examined. These include pillared clay (Vinod and Anirudhan, 2001), sago waste (Quek et al. 1998), cassava waste (Abia et al. 2003), banana pith (Low et al. 1995), peanut skins (Randall et al. 1974), *Medicago sativa* (Alfalfa) (Gardea-Torresdey et al. 1998) and spagnum moss peat (Ho et al. 1995) just to mention a few.

The proximate composition and some surface characteristics essential in assessing the ability of *C. bicolor* as an adsorbent, and the effect of pH on the sorption

*Corresponding author

Table 1. Langmuir adsorption isotherm parameters.

Temp (ºC)	Pb²⁺			Cd²⁺		
	X_m (mg/g)	K	R^2	X_m (mg/g)	K	R^2
30	37.17	0.0393	0.9986	42.19	0.0289	0.9985
40	52.63	0.0380	0.9939	59.02	0.0253	0.9979
50	37.59	0.0263	0.9965	46.95	0.0208	0.9984
60	20.45	0.0260	0.9992	22.47	0.0141	0.9975
70	8.81	0.025	0.9985	14.03	0.0124	0.9944
80	5.49	0.0120	0.9996	8.58	0.0195	0.9956

of Pb^{2+} and Cd^{2+} using *C. bicolor* (Wild Cocoyam) biomass has been reported elsewhere (Horsfall and Spiff, 2004). The data showed that *C. bicolor* is an excellent adsorbent for metal ions in aqueous solutions. In this paper, we report the effect of temperature on the sorption of Pb^{2+} and Cd^{2+} from single metal ion solution using the biomass of *C. bicolor* (Wild Cocoyam) in a temperature range of 30-80ºC.

MATERIALS AND METHODS

Biomass preparation

The plants were harvested and carefully prepared to obtain the biomass as previously reported in our work elsewhere (Horsfall and Spiff, 2004a). A recent screening (Horsfall and Spiff, 2004b) for chemical composition and surface characterization has shown that the major functional groups on *C. bicolor* biomass are polar hydroxyl, aldehydic and carboxylic groups. These groups has made *C. bicolor* to have great potential as an adsorbent for metal ions in aqueous solutions.

Sorption study as a function of temperature

A volume of 50 mL of metal ion solution [Pb^{2+} (from $Pb(NO_3)_2$ and Cd^{2+} (from $Cd(NO_3)_2.4H_2O$)] with varying initial metal ion concentrations of 10 – 100mg/L was placed in a 125 mL conical flask in triplicates. An accurately weighed *Caladium bicolor* biomass sample (250 ± 0.01mg) with particle size of 100 μm was then added to the solution to obtain a suspension. The suspensions were adjusted to pH 5.0. A series of such conical flasks was then

shaken at a constant speed 100 x g in a shaking water bath at temperatures of 30, 40, 50, 60, 70, and 80ºC respectively. After shaking the flasks for 2 hrs, the suspension was filtered using Nº 45 Whatman filter paper and then centrifuge at 2800 x g for 5 min. The supernatants were collected in separate clean test tubes. The metal content at each temperature range was determined using flame atomic absorption spectrometer model A300.

Theory and data evaluation

The mean metal ion sorbed by the biomass at each temperature was determined using a mass balance equation expressed as

$$q_e = \frac{(C_o - C_e)v}{m} \qquad [1]$$

where q_e = metal ion adsorption per unit weight of biomass (mg/g biomass) at equilibrium, C_e = metal ion concentration in solution (mg/L) at equilibrium, C_o = initial metal ion concentration in solution (mg/L), v = volume of initial metal ion solution used (L), m = mass of biomass used (g).

Two models were used to fit the experimental data: Langmuir model and the Freundlich model. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to biomass surface saturation. The linealised form of the above equation after rearrangement is given below:

Table 2. Thermodynamic Parameters for the adsorption of Pb²⁺ and Cd²⁺ on to the biomass of *Caladium bicolor*.

Temp (ºC)	Pb²⁺					Cd²⁺				
	ΔG^o KJ/gmol	E_a KJ/gmol	ΔS^o J/ gmol K	ΔH^o J/gmol	*S x 10^{-4}	ΔG^o KJ/gmol	E_a KJ/gmol	ΔS^o J/ gmol K	ΔH^o J/gmol	*S x 10^{-3}
30	-8.13					-9.40				
40	-8.07					-8.54				
50	-7.66	-16.14	16.06	-9.54	3.86	-7.17	-7.80	7.92	-8.33	7.09
60	-6.57					-6.87				
70	-5.14					-3.87				
80	-2.62					-1.87				

163

Table 3. 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 chemisorption mechanism
S* = 0	Indefinite sticking of adsorbate to adsorbent chemisorption mechanism predominant
0 < S* < 1	Favourable sticking of adsorbate to adsorbent- physisorption mechanism predominant

S*: sticking probability.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad [2]$$

where K_L (dm^3 g^{-1}) is a constant related to the adsorption/desorption energy, and q_{max} is the maximum sorption upon complete saturation of the biomass surface.

The experimental data were fitted into equation [2] for linearisation by plotting C_e/q_e against C_e.

The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass and the linear form is represented by equation 3:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad [3]$$

where; q_e = the metal ion uptake per unit weight of biomass (mg of metal ion adsorbed/g biomass); C_e = Conc. of metal ion in solution at equilibrium (mg dm^{-3}); K_L and n are the Freundlich constants. The value of n indicates the affinity of the sorbent towards the biomass. A plot of ln C_e against

ln q_e in equation [3] yielding a straight line indicates the confirmation of the Freundlich adsorption isotherm. The constants $1/n$ and ln K_L can be determined from the slope and intercept respectively.

In these systems, the Gibbs free energy change is the driving force and the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^o is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, K_o, is given by the following equation:

$$\Delta G^o = -RT \ln K_o \qquad [4]$$

Where ΔG^o is standard free energy of change, J/gmol; R is universal gas constant, 8.314 J/(gmol K); K_o is the thermodynamic equilibrium constant and T is absolute temperature, K. Values of K_o for the sorption process may be determined by plotting $\ln \frac{q_e}{C_e}$ against q_e at different temperatures and extrapolating to zero q_e according to the method of Khan and Singh (1987). The other thermal parameters such as enthalpy change (ΔH^o), and entropy
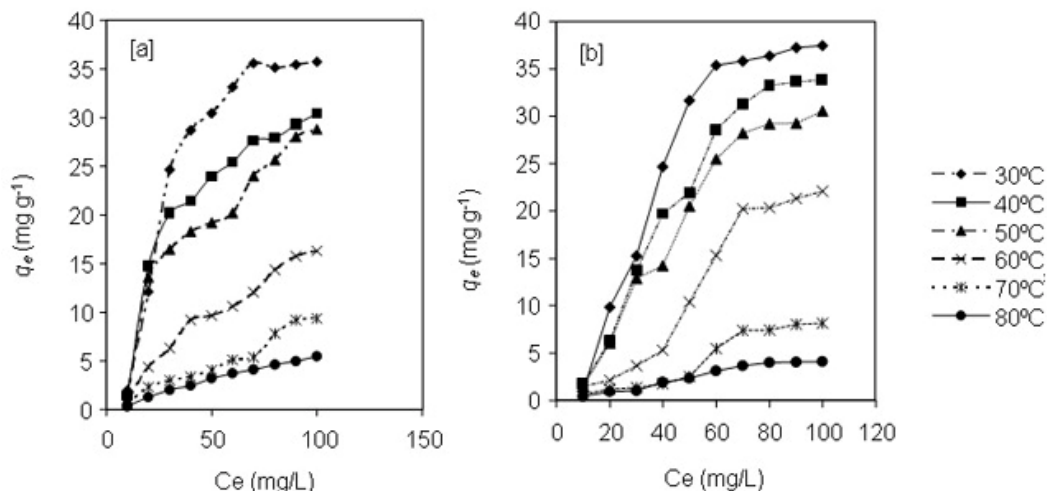

Figure 1. Effect of temperature on the adsorption on to *Caladium bicolor* biomass.
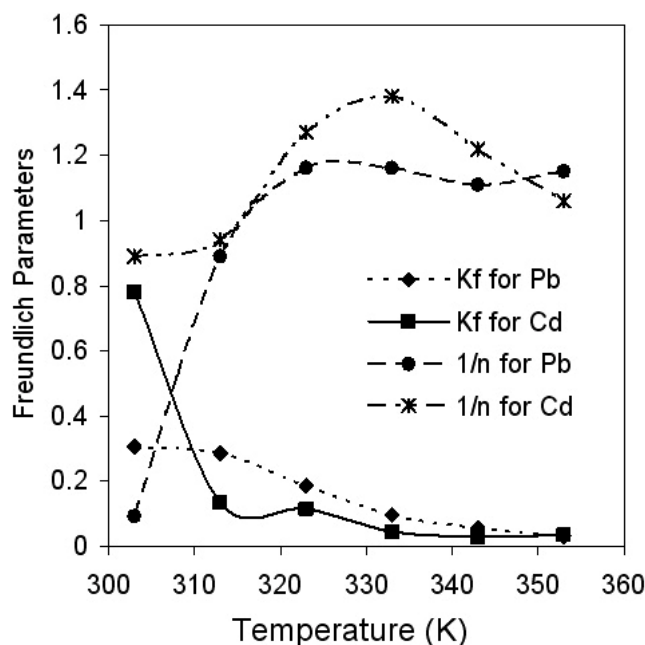(a) Pb^{2+};
(b) Cd^{2+}.

Figure 2. Plots of Freundlich isotherm parameters as a function of temperature.

change (ΔS^o), may be determined using the relationships:

$$\ln K_o = \frac{\Delta S_o}{R} - \frac{\Delta H_o}{RT} \qquad [5]$$

The surface coverage (θ) for studying the sticking probability was calculated from the relation

$$\theta = \left(1 - \frac{C_e}{C_o}\right) \qquad [6]$$

where C_o and C_e are the initial and equilibrium metal ion concentrations respectively.

Statistical analyses were performed using Data Analysis Toolpak Microsoft Excel for Windows 2000 with level of significance maintained at 95% for all tests. One-way analysis of variance (ANOVA) without replication was further used to test the null hypothesis of "no significant differences in the applicability of the C. bicolor biomass towards the sorption of Pb^{2+} and Cd^{2+}".

RESULTS AND DISCUSSION

Effect of temperature

The purpose of this research is to ascertain the effect of temperature on the sorption of metal ion by the non – useful *C. bicolor* biomass plant. The effect of temperature on the removal of Pb^{2+} and Cd^{2+} in aqueous solution by *C. bicolor* biomass was studied by varying the temperature between 30 and 80ºC. The data presented in Figure 1a and 1b showed that adsorption of metal ion by the *C. bicolor* biomass increased with increase in temperature, which is typical for the biosorption of most metal ions from their solution (Manju et al. 1998; McKay et al. 1999; Ho, 2003).

However, the magnitude of such increase continues to decline as temperatures are increased from 30 to 80ºC. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases. Careful examination of the figures revealed that most of the metal ions were removed between
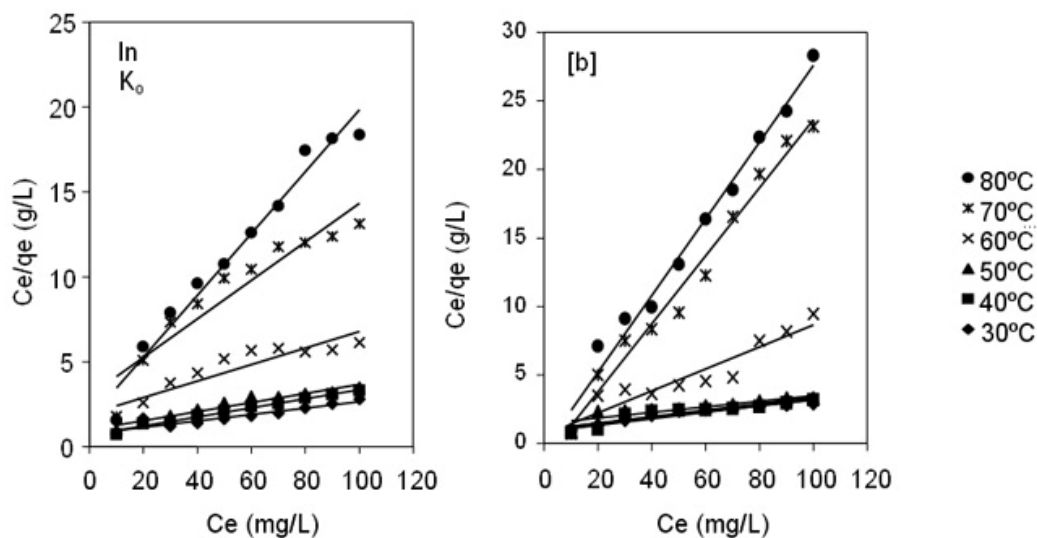

Figure 3. Langmuir isotherm plots for the adsorption onto *Caladium bicolor* biomass.
(a) Pb^{2+};
(b) Cd^{2+}.

the temperatures of 30 to 50ºC. The temperature increases were observed to be in two phases for lower temperatures and three phases for higher temperatures. For lower temperatures, equilibrium sorption occurs rapidly at lower metal ion concentrations in the first phase and becomes relatively constant at higher concentrations. The equilibrium concentration was obtained at 50 mg/L for Pb^{2+} and 70 mg/L for Cd^{2+}. As temperature increased above 50ºC, an initial slow sorption was observed followed by a rapid sorption process to reach equilibrium and a relatively constant sorption process in the third and final phase. The equilibrium concentrations for higher temperatures (60-80ºC) were not significantly different for those of lower temperatures. This indicates that increasing the initial metal ion concentrations above the equilibrium concentrations of 50 – 70 mg/L may not have any significant increase in the sorption of metal ions by *C. bicolor* biomass.

At high temperature, 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).

The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between biomass surface and the metal ion, which supports physisorption. According to Giles classification as reported by Vinod and Anirudhan (2001), the adsorption isotherms for all temperatures may be further classified into several subgroups of I, II, III, etc according to the shape of the curves. The sorption isotherms at 10-40ºC belong to the subgroup III of Giles classification. On the other hand, the

sorption isotherms at 50-60ºC belongs to subgroup II, while above 70ºC is subgroup I. In this investigation temperatures of 30 and 45ºC in Figure 1 tend to define a plateau; therefore it seems reasonable to support the proposal that for the experimental conditions used, the formation of a complete monolayer of metal ion covering the biomass surface belongs to subgroup III, meaning that saturation of the biomass surface seems to be reached at 10 to 40ºC and the optimal temperature of adsorption for Pb^{2+} and Cd^{2+} could be obtained within this range.

To facilitate the estimation of the adsorption capacities at various temperatures, experimental data were fitted into equilibrium adsorption isotherm models of Freundlich and Langmuir.

Sorption data were fitted by Freundlich adsorption isotherm at all temperatures (r^2 were greater than 0.94). The Freundlich adsorption isotherm parameters, $1/n$ and K_F, were then plotted against temperature (Figure 2). The values of $1/n$ were found to be more than unity at all temperatures except 30 and 40ºC, indicating that desorption occurs at above 40ºC. This implies that significant adsorption took place at low temperatures, which becomes less significant at higher temperatures. The ultimate adsorption capacity of the biomass at the different temperatures can be calculated from the isothermal data by substituting the required equilibrium concentration in the Freundlich equation. The value of K_F, which is a measure of the degree of adsorption, decreases with increase in temperature (Figure 2). The higher K_F values at lower temperatures indicate that more sorption would be expected at these temperatures.
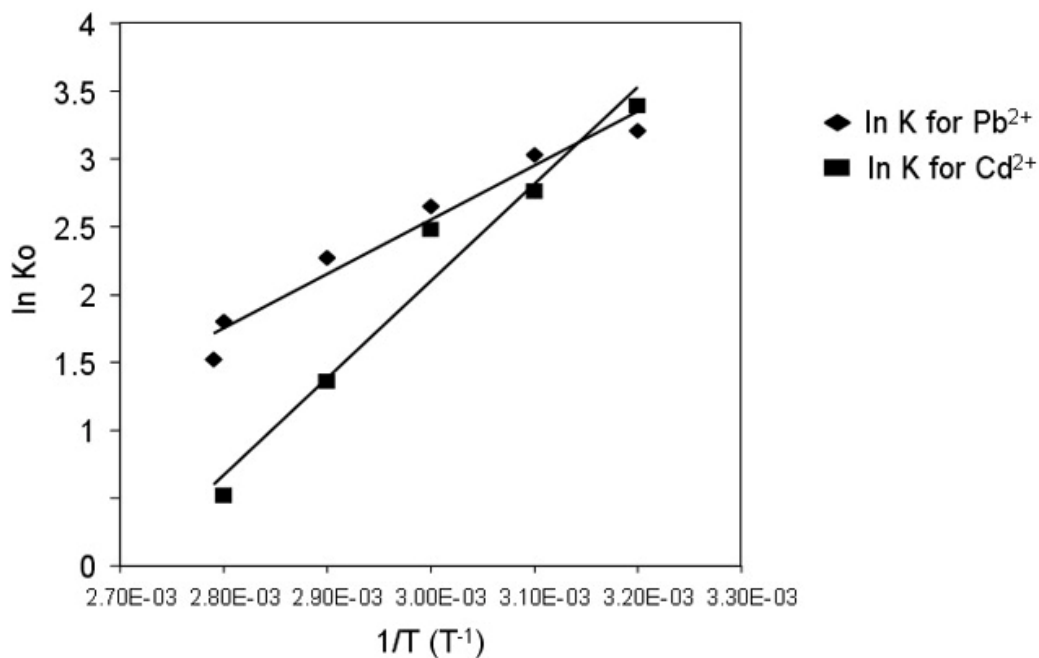

Figure 4. Plot of lnK_o against reciprocal temperature for Pb^{2+} and Cd^{2+} sorption on *Caladium bicolor* biomass.

The most probable temperature of adsorption was further evaluated by the Langmuir isotherm. The Langmuir maximum adsorption, X_m, for a monomolecular surface coverage and the adsorption equilibrium constants, K_F, at the temperatures investigated were obtained from the plot (Figure 3) for the prediction of the probable temperature of adsorption. Relevant parameters values as shown in Table 1 indicate that optimal temperature of adsorption in utilizing *Caladium bicolor* biomass for the removal of metals in aqueous solutions is about 40ºC. The Langmuir fits at all temperatures show slight curvatures (Figure 3), which suggest that the surface adsorption is not a single monolayer with single sites. Two or more sites with different affinities and maximum may be involved in metal ion sorption. After 40ºC, the values of X_m and K decreased with increase in temperature, showing that adsorption capacity and intensity of adsorption are enhanced at lower temperatures.

Furthermore, the coefficients of determination, R^2, from the Langmuir model was subjected to the one-way analysis of variance (ANOVA) at $\alpha = 0.05$ to test the null hypothesis (h_o) of no significant difference in the applicability of *C. bicolor* to remove Pb^{2+} and Cd^{2+} from aqueous solution. The statistical data obtained showed that $F_{cal}(0.47) \ll F_{crit}$, (4.39), hence, we accept the h_o, which indicates that the *C.*

bicolor had similar sorption potential for the removal of Pb^{2+} and Cd^{2+} from aqueous effluent .

Thermodynamic treatment of the sorption process

The thermodynamic treatment of the sorption data indicates that ΔG^o values were negative at all the temperatures investigated. The negative values of ΔG^o (Table 2) indicate the spontaneous nature of adsorption of metal ion by the biomass. It is of note that ΔG^o up to -20 KJ gmol^{-1} are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption) while ΔG^o values more negative than -40 KJ gmol^{-1} involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption). The ΔG^o values obtained in this study for both metal ions are < -10 KJ gmol^{-1}, indicative that physical adsorption is the predominant mechanism in the sorption process. The values of (ΔH^o) and (ΔS^o) were obtained from the slope and intercept of plots of ln K_o vs 1/T (Figure 4) and are shown in Table 2. The negative values of (ΔH^o) for Pb^{2+} and Cd^{2+} on to the biomass further confirm the exothermic nature of the adsorption process. The positive values of ΔS^o (Table 2) show that the freedom of metal ions is not too restricted in the biomass confirming a physical adsorption, which is further confirmed by the relatively low values of ΔG^o.
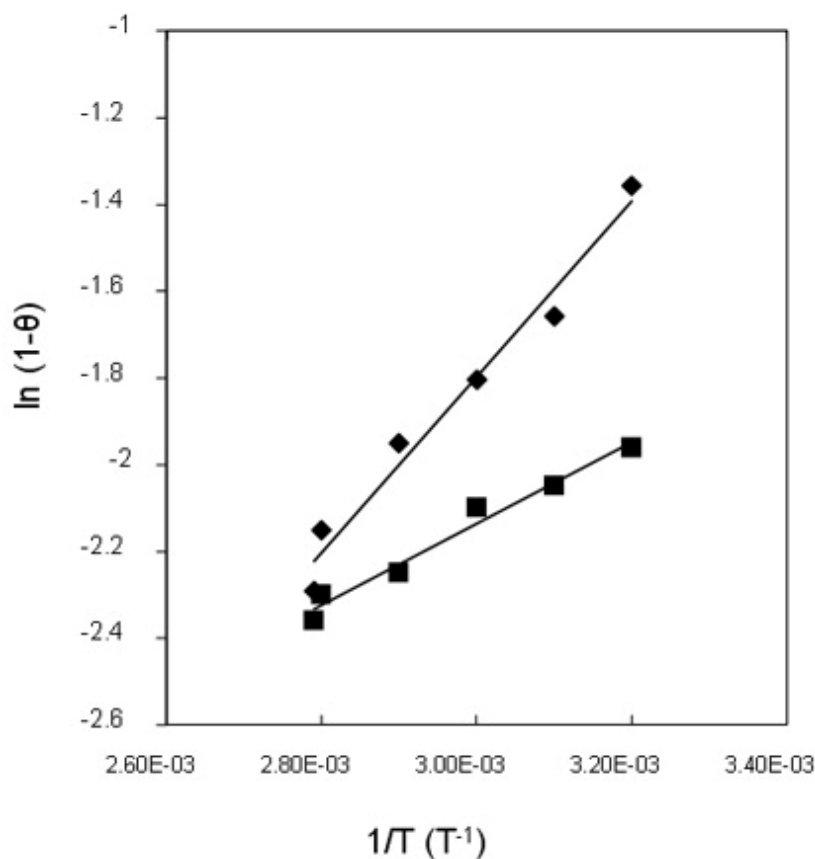

Figure 5. The relationship between temperature and sticking probability for Pb^{2+} and Cd^{2+} sorption on *Caladium bicolor* biomass.

In order to further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage as expressed in equation 7:

$$S^* = (1-\theta)\exp-\left(\frac{E_a}{RT}\right) \qquad [7]$$

The sticking probability, S^*, is a function of the adsorbate/adsorbent system under consideration but must lie in the range $0 < S^* < 1$ and is dependent on the temperature of the system. The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 3.

The effect of temperature on the sticking probability was evaluated throughout the temperature range from 30 to 80ºC by calculating the surface coverage at the various temperatures. The plot of $\ln(1-\theta)$ against 1/T gave linear plots with intercept of $\ln S$ and slope of E_a/R as shown in Figure 5. The apparent activation energy (E_a) and the sticking probability (S^*) are estimated from the plot with reasonable good fit for the two metal ions on the biomass ($r^2 > 0.97$). The E_a values calculated from the slope of the plot were found to be –16.14 KJ gmol^{-1} and – 7.92 KJ gmol^{-1} for Pb^{2+} and Cd^{2+} respectively. The negative values of E_a indicate that lower solution temperatures favours metal ion removal by adsorption onto the *Caladium bicolor* biomass and the adsorption process is exothermic in nature. Relatively low values of E_a suggests that metal ion adsorption is a diffusion controlled process. The results as shown in Table 2 indicate that the probability of metal ion sticking to the *C. bicolor* biomass surface is very high as $S^* \ll 1$ for both metals (Table 2). These values confirm that, the sorption process is physisorption.

CONCLUDING REMARKS

In conclusion, the results clearly establish that the sorption of Pb^{2+} and Cd^{2+} onto *C. bicolor* is favoured at lower solution temperatures. The range of temperatures which favours the adsorption process was 10-45ºC with optimal temperature at 40ºC. This temperature range is favourable for solubility of chemicals in wastewater treatment systems and will also enhance the reaction rates. The activation energy further supports lower solution temperatures and an excellent sticking of metal ions on to *C. bicolor* biomass. The sorption process is spontaneous and exothermic and the mechanism is physisorption. The equilibrium data agrees with the Langmuir isotherm. The sorption capacity of Cd^{2+} is higher than Pb^{2+} because of the ionic sizes of the ions; however, there is no significant difference in the sorption potential of the biomass towards the two metal ions in aqueous solution. *Caladium bicolor* is a non-useful plant growing in the wild. Its use as an adsorbent may eventually encourage cultivation of the plant and enhance the economies of local farmers and generate employment. The biomass from *C. bicolor* may be recycled and the recovered biomass is biodegradable and therefore environment friendly. Hence, not only is *C. bicolor* waste inexpensive and readily available, it also has the potential for metal removal and recovery of metal ions from contaminated waters. This process will be environment friendly and reduce the huge amount of indiscriminate effluent discharges all around the small industry concerns in Nigeria. It may also provide an affordable technology for small and medium-scale industry in Nigeria.

REFERENCES

ABIA, A.A.; HORSFALL, M. Jnr and DIDI, O. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. *Bioresource Technology*, 2003, vol. 90, no. 3, p. 345-348.

AKSU, Z. and KUTSAL, T.A. A bioseparation process for removing Pb(II) ions from wastewater by using *C. vulgaris*. *Journal Chemical Technology and Biotechnology*, 1991, vol. 52, no. 1 p. 108-118.

GARDEA-TORRESDEY, J.L.; GONZALEZ, J.H.; TIEMANN, K.J.; RODRIGUEZ, O and GAMEZ, G. Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa). *Journal of Hazardous Materials*, 1998, vol. 57, no. 1-3, p. 29-39.

HO, Y.S. Removal of copper ions from aqueous solution by tree fern. *Water Research*, 2003, vol. 37, no. 10, p. 2323-2330.

HO, Y.S.; JOHN WASE, D.A. and FORSTER, C. F. Batch nickel removal from aqueous solution by spagnum moss peat. *Water Research*, 1995, vol. 29, no. 5, p. 1327-1332.

HORSFALL, M. Jnr and SPIFF, A.I. Adsorption of metal Ions from mixed metal solutions on *Caladium Bicolor* (wild cocoyam) biomass surface. *Journal of Corrosion Science and Technology,* 2004a, vol. 2, p. 12-18.

HORSFALL, M. Jnr and SPIFF, A.I. Studies on the effect of pH on the sorption of Pb^{2+} and Cd^{2+} ions from aqueous solutions by *Caladium bicolor* (wild cocoyam) biomass. *Electronic Journal of Biotechnology* [online]. 15 December 2004b, vol. 7, no. 3. Available from Internet: http://www.ejbiotechnology.info/content/vol7/issue3/full/8/index.html. ISSN 0717 3458.

KHAN, A.A and SINGH, R.P. Adsorption thermodynamics of carbofuran on Sn(IV) arsenosilicate in H$^+$, Na$^+$ and Ca^{2+} forms. *Journal of Colloid Science*, 1987, vol. 24, no. 1, p. 33-42.

LOW, K.S.; LEE, C.K. and LEO, A.C. Removal of metals from electroplating wastes using banana pith. *Bioresource Technology*,1995, vol. 51, no. 2-3, p. 227-231.

MANJU G.N.; RAJI, C. and ANIRUDHAN, T.S. Evaluation of coconut husk carbon for the removal of arsenic from water. W*ater Research*, 1998, vol. 32, no. 10, p. 30662-30670.

MCKAY G.; HO, Y.S. and NG, J.C.P. Biosorption of copper from waste water: a review. *Separation and Purification Methods*, 1999, vol. 28, no. 1, p. 87-125.

QUEK, S.Y.; WASE, D.A.J. and FORSTER, C.F. The use of sago waste for the sorption of lead and copper. *Water SA*,1998*,* vol. 24, no. 3, p. 251-256.

RANDALL, J.M.; REUTER, F.C and WAISS, A.C. Removal of cupric ions from solution by contact with peanut skins. *Journal of Applied Polymer Science*, 1974, vol. 19, p. 156-171.

TSEZOS, M. and VOLESKY, R.P. Biosorption of uranium and thorium. *Journal of Biotechnology and Bioengineering*, 1987, vol. 23, p. 583-604.

VINOD, V.P. and ANIRUDHAN, T.S. Sorption of tannic acid on zirconium pillared clay. *Journal of Chemical Technology and Biotechnology*, 2001*,* vol. 77, p. 92-101.

Note: Electronic Journal of Biotechnology is not responsible if on-line references cited on manuscripts are not available any more after the date of publication. Supported by UNESCO / MIRCEN network.

169