

Kinetic, Equilibrium and Thermodynamic Studies of the Biosorption of Ni(II), Cr(III), and Co(II) from Aqueous Solutions using Cocoyam (*Colocasia esculenta*) Leaf.

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ABSTRACT

The biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam (*Colocasia esculenta*) leaf is reported in this work. The effects of solution pH, contact time, initial metal ion concentration, and temperature on the biosorption of the metal ions were investigated. Optimum pH for each metal ion was obtained as the biosorption of each of the metal ions was found to be pH-dependent. Kinetic study shows that the pseudo-second-order kinetic model best represents the biosorption of the metal ions. The sorption of each metal ion was analyzed with Freundlich and Langmuir isotherm models, in each case, the Freundlich model appears to have better regression coefficients than the Langmuir model. The study on the effect of dosage shows that the dosage of the biomass significantly affects the uptake of the metal ions from solution.

Thermodynamically, the biosorption of each of each of Ni(II) and Cr(III) is endothermic while that of Co(II) is exothermic. The biosorption of each metal ion is spontaneous and the order of spontaneity of the biosorption process being Co(II)>Ni(II)>Cr(III). Similarly, positive change in entropy was observed for each and the order of disorder is Ni(II)>Co(II) >Cr(III).

(Keywords: biosorption, cocoyam, Ni(II), Cr(III), Co(II))

INTRODUCTION

Important metals such as nickel, chromium and cobalt from industrial processes like mining operations, sludge disposal, metal plating and manufacture of electrical equipment are released into the environment as effluents. They invariably

become pollutants of the environment. The toxic nature of these pollutants has caused increased concern for their removal from industrial effluents.

Biosorption has been found to be an efficient and effective alternative technology at little or no cost compared with the conventional methods of removing them from effluents which are rather expensive with associated demerits. Various agricultural wastes have been investigated for their potentials to remove these metal ions from solution in order to determine their possible application in treating industrial effluents containing metal ions [Babarinde et al., 2008a; 2008b; 2008c; 2009; 2010a; 2011; Basu et al., 2010; Chakravarty et al., 2010; Fiorrentin, 2010; García-Rosales and Colín-Cruz., 2010; Liu et al., 2010; Qu et al., 2010; Vijayaraghavan,2010; Zhang and Wang,2010; Uluozlu, 2010].

Cocoyam (*Colocasia esculenta*) is a plant that is grown across the tropics for its tuber. However, the leaf is unutilized thereby becoming an environmental nuisance. It is found to contain abundant functional groups such as hydroxyl, amino and carbonyl groups which contain lone pairs of electrons needed for biosorption of cationic pollutants in solution. It was on this basis that this readily available agricultural waste was investigated for its potential in treating industrial effluents containing Ni(II), Cr(III), and Co(II).

METHODOLOGY

Biomass Preparation

Cocoyam (*Colocasia esculenta*) leaves were harvested from a farm near the mini campus of

Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria. The leaves were properly rinsed with water, sun dried immediately and later cut into pieces of approximately 0.5cm. The leaf sample was kept dry till time of usage.

Preparation of Solution

All chemicals used in this study were of analytical reagent grade and were used without further purification. Standard solutions of Ni(II), Cr(III), and Co(II) used for the study were prepared from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, respectively. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution immediately prior to their use with distilled water.

The initial pH of the solution was adjusted accordingly with a pH meter. A thermostated water bath (Haake Wia Model) was used as the medium for the process. The concentration before and after biosorption of each metal ion was determined using a Perkin-Elmer Analyst 700 flame atomic absorption spectrophotometer with deuterium background corrector. Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and metal loaded biomass were recorded at $400\text{-}4000\text{ cm}^{-1}$ using a Shimadzu FT-IR model 8400S spectrophotometer.

Batch Biosorption Study

The biosorption study was carried out by contacting 0.5g of the Cocoyam (*Colocasia esculenta*) leaf with 25ml of the metal ion solution under different conditions for a period of time in a boiling tube. The biosorption studies were conducted at 27°C using thermostated water bath to determine the effect of pH, contact time and initial metal ion concentration on the biosorption. The residual metal ion was analyzed using Atomic Absorption Spectrophotometer. The amount of metal ion biosorbed from solution was determined by difference and the mean value calculated.

Effect of pH on biosorption

The effect of pH on the biosorption of the metal ion was carried out within the range that would not be influenced by the metal precipitated. This was done by contacting 0.5g of banana leaf with 25ml

of 100 mgL^{-1} metal ion solution in a boiling tube within the range pH 1- 7. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1M HNO_3 and/or 0.1M NaOH. The boiling tubes containing the mixture were left in a water bath for 6 hours. The biomass was removed from the solution by decantation. The residual metal ion concentration in the solution was analyzed. The optimum pH was determined as the pH with the highest biosorption of each metal ion.

Effect of Contact Time on Biosorption

The biosorption of the metal ions by Cocoyam (*Colocasia esculenta*) leaf was studied at various time intervals (0-360 min) and at the concentration of 100 mg L^{-1} . This was done by weighing 0.5g of Cocoyam (*Colocasia esculenta*) leaf into each boiling tube and 25ml of 100 mg L^{-1} of metal ion solution at optimal pH was introduced into it. The leaf was left in solution for varying periods of time. The solution in the boiling tube was decanted at different time intervals from the first to the last tube. The aliquot was then taken for analysis using an Atomic Absorption Spectrophotometer. The amount of metal ions biosorbed was calculated for each sample.

Effect of Initial Metal Ion Concentration on Biosorption

Batch biosorption study of metal ion was carried out using a concentration range of $10\text{-}300\text{ mgL}^{-1}$. This was done by introducing 0.5 g of the Cocoyam (*Colocasia esculenta*) leaf into each of the boiling tubes employed and 25 ml of 100 mgL^{-1} of metal ion solution at optimal pH was added to the tube. Two boiling tubes were used for each concentration. The tubes were left in a thermostated water bath maintained at 27°C . The metal bound Cocoyam (*Colocasia esculenta*) leaf was removed from the solution and the concentration of residual metal ion in each solution was determined.

Effect of Temperature on Biosorption

The batch biosorption process was studied at different temperatures of $20\text{ - }50^\circ\text{C}$ in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.5 g of banana leaf with 25ml of 100 mgL^{-1} of

metal ion solution at the optimal pH. The biosorption of metal ion may involve chemical bond formation and ion exchange since the temperature is a main parameter affecting them.

Statistical Analyses

The curve fittings of the data obtained were performed using Microcal Origin 6.0 software.

RESULTS AND DISCUSSION

FT-IR Studies of the Free and Metal-Bound Cocoyam Leaf

The FT-IR spectra of dried unloaded, Ni-loaded, Cr-loaded and co-loaded Cocoyam (*Colocasia esculenta*) leaf were taken to obtain information on the nature of possible interactions between the functional groups of cocoyam leaf biomass and the metal ions as presented in Figure 1.

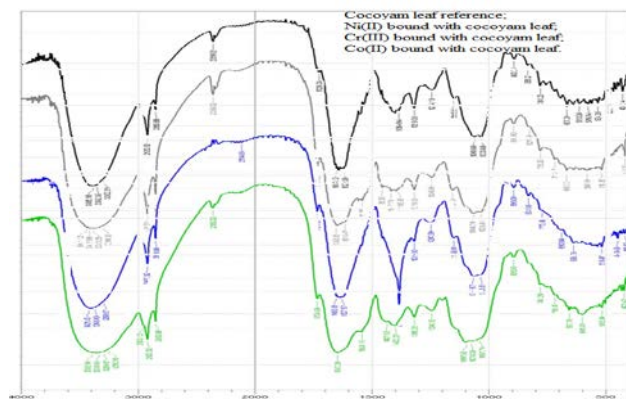


Figure 1: FT-IR Spectra of the Free and Metal-Bound Cocoyam Leaf.

The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the –OH and C=O groups as shown in Figure 1. These bands are due to the functional groups of Cocoyam (*Colocasia esculenta*) leaf that participate in the biosorption of Ni(II), Cr(III) and Co(II). On comparison, there are clear band shifts and decrease in intensity of bands as reported in Table 1.

The FT-IR spectra of the Cocoyam (*Colocasia esculenta*) leaf biomass indicated slight changes in the absorption peak frequencies due to the fact

that the binding of the metal ions causes reduction in absorption frequencies. These shifts in absorbance observed implies that there were metal binding processes taking place on the active sites of the biomass.

Analysis of the FT-IR spectra showed the presence of ionizable functional groups (C=O, O-H) which are able to interact with cations [Uluozlu, 2010; Pradhan, et al., 2007; Bueno et al., 2008; Sun et al., 2008; Ertugay et al., 2008]. This implies that these functional groups would serve in the removal of positively charged ions from solution.

Effect of Solution pH on Metal ion Biosorption

The pH of solution has been established to be a vital parameter in biosorption process [Sun et al., 2008; Babarinde, 2011]. The net charge of the sorbate and that of the sorbent are dependent on the pH of the solution. At low pH, the metal ion uptake is inhibited by net positive charge on the sorbent and the competition between the metal ions and the hydrogen ions in solution. As the pH increases, the negative charge density on biomass increases as a result of deprotonation of the metal binding sites on the leaf, consequently, the biosorption of the metal ions increases.

Figure 2 shows the variation of the metal ion biosorbed on Cocoyam (*Colocasia esculenta*) leaf at various solution pH values. In each case, the biosorption increased steadily as the pH increased from pH 1 to pH 6. The increase observed in the biosorption with increase in pH implies that ion-exchange process is involved. The reaction involved the biosorption of metal ion (represented as M^{x+} for a metal ion) from the liquid phase to the solid phase, the biosorbent with lone pair of electrons (represented as \ddot{A}), and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below for a divalent metal ion in solution:



The reversibility of the biosorption process is observed when the metal-bound biomass is treated with dilute HNO_3 which is a desorption process.

Table 1: FT-IR Spectra Characteristics of Cocoyam Leaf Before and After Biosorption of Ni(II), Cr(III), and Co(II) for 2 hours.

IR band peak	Absorption bands (cm ⁻¹)			Functional groups
	Before	After	Difference	
Ni(II)	3385.18	3441.12	55.94	O-H stretch
Cr(III)	3385.18	3421.83	36.65	O-H stretch
Co(II)	3385.18	3332.39	-52.79	O-H stretch
Ni(II)	2850.88	2920.32	69.44	C-H
Cr(III)	2850.88	2850.88	-	C-H
Co(II)	2850.88	2850.88	-	C-H
Ni(II)	1726.12	1734.06	7.94	C=O stretch
Cr(III)	1726.12	1734.06	7.94	C=O stretch
Co(II)	1726.12	1734.06	7.94	C=O stretch
Ni(II)	1651.12	1653.05	1.93	C=C stretch
Cr(III)	1651.12	1653.05	1.93	C=C stretch
Co(II)	1651.12	1543.10	-108.02	C=C stretch
Ni(II)	1384.94	1541.18	156.24	C-H bend
Cr(III)	1384.94	1384.94	-	C-H bend
Co(II)	1384.94	1400.37	15.43	C-H bend
Ni(II)	1060.88	1064.74	3.86	C-O stretch
Cr(III)	1060.88	1066.67	5.79	C-O stretch
Co(II)	1060.88	1037.74	-23.14	C-O stretch
Ni(II)	667.39	669.32	1.93	C-X stretch
Cr(III)	667.39	638.46	-28.93	C-X stretch
Co(II)	667.39	657.75	-9.64	C-X stretch

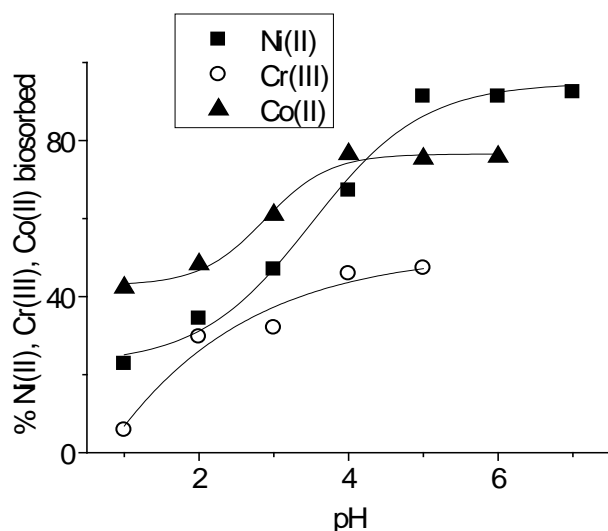


Figure 2: pH-Dependent Profile of the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf.

Biosorption kinetics

Figure 3 illustrates the dynamic biosorption process of the three metal ions on Cocoyam (*Colocasia esculenta*) leaf. It is observed that the

biosorptive quantities of the three metal ions on Cocoyam (*Colocasia esculenta*) leaf increase with increasing contact time.

In each case, biphasic kinetics is observed: an initial rapid stage (fast phase) where biosorption is fast and contributes to equilibrium uptake and a second stage (slow phase) whose contribution to the metal ion biosorption is relatively smaller.

The fast phase is the instantaneous biosorption stage, it is assumed to be caused by external biosorption of metal ion to the leaf surface. The second phase is a gradual biosorption stage, which is diffusion rate controlled. Finally, the biosorption sites are used up, the uptake of the metal ion reached equilibrium. This phase mechanism has been suggested to involve two diffusion processes, external and internal, respectively [Wu et al., 2010].

The biosorption of each of the three metal ions achieves equilibrium within 3 hr although their rates of uptake are different. This might be due to the differences in hydrated ionic sizes of the metal ions [Kielland, 1937].

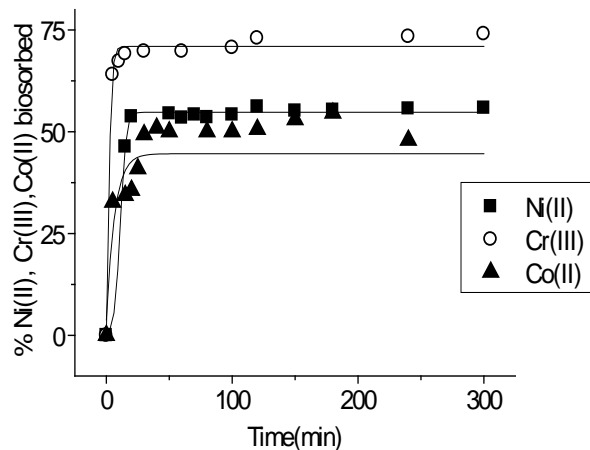


Figure 3: Time Course of the Biosorption of Ni(II), Cr(III), and Co(II) by cocoyam leaf.

Several kinetic models are needed to establish the mechanism of a biosorption process [Okasha et al., 2010]. In order to investigate the kinetics of the biosorption of these metal ions on Cocoyam (*Colocasia esculenta*) leaf, four kinetic models were employed. These are the pseudo-first-order, the pseudo-second-order, the Elovich and the Intraparticle equations. One of such models is the Lagergren pseudo-first-order model which considers that the rate of occupation of the biosorption sites is proportional to the number of the unoccupied sites [Ertugay and Bayhan , 2008]:

$$\text{rate} = -\frac{d[A]}{dt} = k [A]^n \quad (2)$$

Which can also be written as:

$$\frac{d}{dt} q_t = k_1 (q_e - q_t) \quad (3)$$

Integrating between the limits $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, we obtain:

$$\log \left[\frac{q_e}{(q_e - q_t)} \right] = \frac{k_1}{2.303} t \quad (4)$$

This can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

where k_1 is the Lagergren rate constant of the biosorption (min^{-1}); q_e and q_t are the amounts of metal ions sorbed (mg g^{-1}) at equilibrium and at time t , respectively. The plot of $\log(q_e - q_t)$ versus t for the biosorption of metal ions on the biomass at initial concentration of 100 mg L^{-1} should give a straight line for a process that follows first-order kinetic model. The data was equally subjected to the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is represented as:

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

On integrating between boundary conditions, we have:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (7)$$

On rearrangement, we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where k_2 is the equilibrium rate constant of pseudo-second-order biosorption process ($\text{g mg}^{-1} \text{ min}^{-1}$). In the three metal ions under study, the straight line plots of t versus t/q_t showed good fitness of experimental data with the second-order kinetic model for different initial concentration of the three metal ions as presented in Figure 4.

The data were equally subjected to the Elovich kinetic model given by:

$$q_t = A + B \ln t \quad (9)$$

The intraparticle diffusion equation given as:

$$R = K_s t^b \quad (10)$$

has been used to indicate the behaviour of intraparticle diffusion as the rate limiting step in the biosorption process. R is the percent metal biosorbed, K_s is the intraparticle diffusion constant, t is the contact time, while b is the gradient of the linear plot. In the linear form, equation (10) turns to:

$$\log R = b \log t + \log K_s \quad (11)$$

Out of the four kinetic models tested, the correlation coefficients were found to be highest for the pseudo-second-order kinetic equation and in each case it is in excess of 0.99 as presented in Table 2.

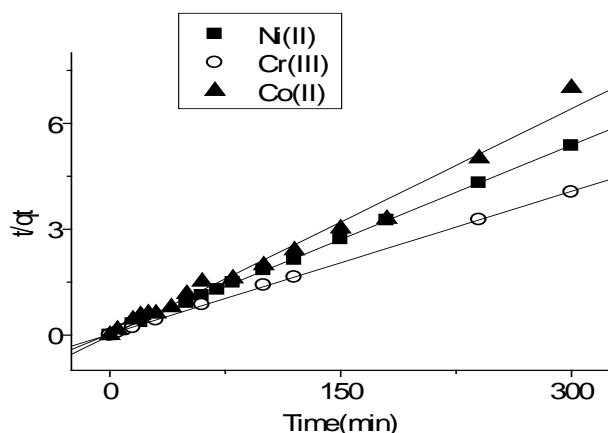


Figure 4: The Pseudo-Second-Order Kinetic Plot for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf at 27°C.

The pseudo-second-order kinetic model is the best kinetic model to predict the dynamic biosorption of Ni(II), Cr(III), and Co(II) on Cocoyam (*Colocasia esculenta*) leaf. The result shows that the rate of biosorption of the metal ions is of the order Ni(II)>Cr(III)> Co(II) which may be due to the differences in hydrated ionic sizes of

the ions in solution [Kielland, 1937]. The biosorption capacity is in the order Cr(III)>Ni(II)>Co(II). This implies that the amount of each metal biosorbed depends on its valency.

Biosorption Isotherm

Figure 5 illustrates the biosorption isotherm of Ni(II), Cr(III) and Co(II) on Cocoyam (*Colocasia esculenta*) leaf. The equilibrium biosorption q_e increases with increase in metal ion concentration. The Freundlich and Langmuir isotherms, were employed to calculate the biosorption capacity. The Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface. The Freundlich isotherm is expressed as:

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \quad (12)$$

Where K_f and $\frac{1}{n}$ are the Freundlich constants related to the biosorption capacity and biosorption intensity of the biosorbent, respectively.

The linear form of the Langmuir equation is expressed as:

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \quad (13)$$

Where Γ , Γ_m and b_m are the Langmuir parameters. The parameters of the Langmuir isotherms show that the Langmuir isotherm is a better isotherm than the Freundlich isotherm and are presented in Table 3.

Table 2: Parameters of the Pseudo-Second-Order Kinetic Model for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf.

Metal ion	k_2 (g.mg ⁻¹ .min ⁻¹)	q_e (mg g ⁻¹)	R ²	S.D.
Ni(II)	8.813x10 ⁻³	56.11	0.9998	0.0233
Cr(III)	7.89 x10 ⁻³	74.074	0.9997	0.0221
Co(II)	3.405 x10 ⁻³	52.083	0.9885	0.1535

Table 3: Freundlich Isothermal Parameters for the Biosorption of Ni(II), Cr(III), and Co(III) by Cocoyam (*Colocasia esculenta*) Leaf.

Metal ion	Freundlich parameters			
	1/n	K _f	R ²	S.D.
Ni(II)	3.0896	0.0113	0.9977	0.0255
Cr(III)	5.0386	7.2127	0.7939	0.1274
Co(II)	1.295	0.4046	0.987	0.0583

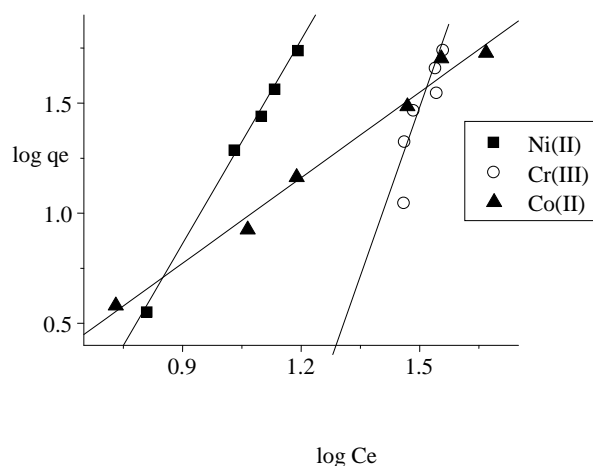


Figure 5: Freundlich Isotherm for Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam (*Colocasia esculenta*) Leaf.

The K_f values show that the uptake of the metal ions is of the order Cr(III) > Co(III) > Ni(II). This implies that the valency as well as the hydrated ionic sizes of the metal ions affect their biosorption.

Biosorption Efficiency

The result of the study on the effect of initial metal ion concentration on biosorption efficiency is shown in Figure 6. The plots show that the biosorption efficiency of the biomass increases with increase in the initial metal ion concentration of for all the metal ions which might be due to increase in effective collision between the metal ions and the active sites. Similar trend has been observed for the biosorption of Pb(II) by *Calymperes erosum* [Babarinde et al., 2010b]. The biosorption efficiency (E) for each metal ion was calculated as:

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \quad (14)$$

Where C_i and C_e are the initial and the equilibrium metal ion concentrations (mg L⁻¹), respectively.

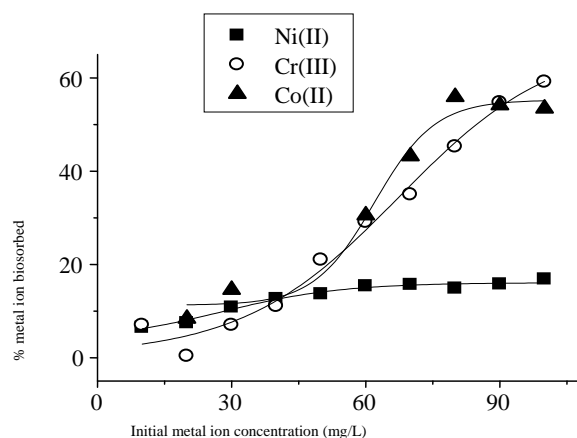


Figure 6: Effect of Initial Metal Ion Concentration on the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam (*Colocasia esculenta*) Leaf.

Effect of Biomass Dosage on Biosorption

The effect of biomass dosage on biosorption efficiency is reported in Figure 7. The general trend of increase in metal ion biosorbed with increase in biomass dosage indicates an increase in uptake due to more binding sites on the biomass available for biosorption. Such trend has been reported for other biosorbents [Babalola et al., 2009].

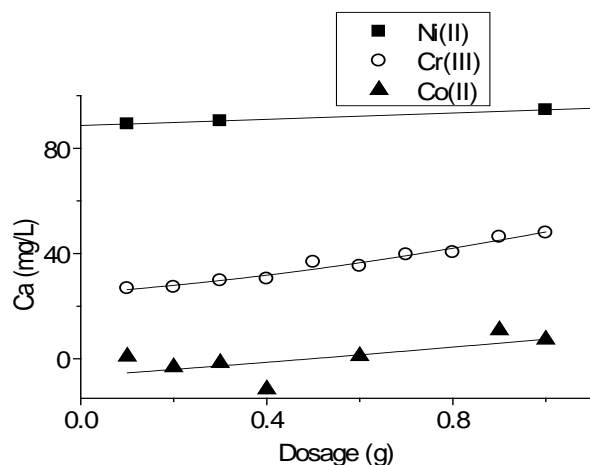


Figure 7: Effect of Dosage on the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf.

Biosorption Thermodynamics

The variation of temperature affects the biosorption of metal ions onto solid surfaces of biomass since the biosorption process is a reversible one. The nature of each side of the equilibrium determines the effect temperature has on the position of equilibrium. The side that is endothermic is favored by increase in temperature while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation [de la Rosa et al., 2008; Sun et al., 2008].

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

Where T (K) is the absolute temperature. The equilibrium constant (K_c) was calculated from the following relationship.

$$K_c = \frac{C_{ad}}{C_e} \quad (16)$$

Where C_e and C_{ad} are the equilibrium concentrations of metal ions (mg L^{-1}) in solution and on biosorbent, respectively. Consequently, the thermodynamic behavior of the biosorption of Ni(II), Cr(III) and Co(II) onto cocoyam leaf was evaluated through the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The thermodynamic parameters like enthalpy and entropy are obtained using van't Hoff equation [Uluozlu et al., 2010; Qu et al., 2010]. The change in free energy is related to other thermodynamic properties as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

Where T is the absolute temperature (K); R is the gas constant ($8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$). ΔH° ($\text{J} \cdot \text{mol}^{-1}$) and ΔS° ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) were calculated from the slope and intercept of the linear plot of $\ln K_c$ vs $1/T$. The thermodynamic parameters obtained for this study are presented in Table 4. The plots shown in Figure 8 are linear over the entire range of temperature investigated.

Table 4: Thermodynamic Parameters for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf.

Metal ion	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	R ²	S.D.
Ni(II)	13.992	63.77	0.9937	54.52
Cr(III)	9.501	28.13	0.9610	66.97
Co(II)	-0.62	40.12	0.9610	118.90

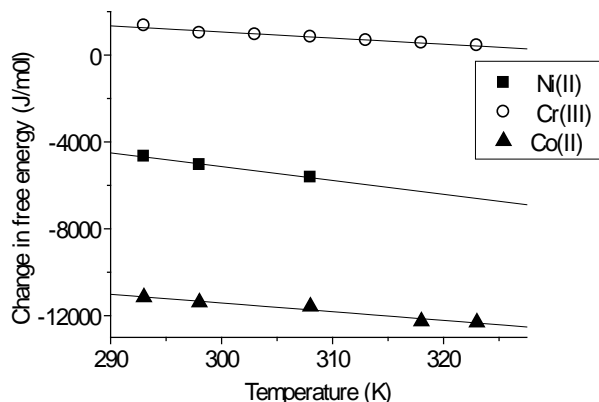


Figure 8: Thermodynamic Plots for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoyam Leaf.

The negative values of ΔG° indicate spontaneity of each biosorption process, with the order of spontaneity being $\text{Co(II)} > \text{Ni(II)} > \text{Cr(III)}$. The positive values of ΔH° for the biosorption of Ni(II) and Cr(III) the three metal ions suggest endothermic nature of the biosorption processes while that of Co(II) is exothermic. This is also supported by the increase in the value of biosorption capacity of the biosorbent with rise in temperature. The positive value of ΔH° indicates the presence of an energy barrier in the biosorption process. Similarly, the ΔS° values are positive indicating increase in randomness during the biosorption process for these three metal ions. These positive values of ΔS° observed for the biosorption of these metal ions indicates an increase in randomness at the solid/solution interface during their biosorption. The order of increasing disorder being $\text{Cr(III)} < \text{Co(II)} < \text{Ni(II)}$.

CONCLUSIONS

In this work we have studied the biosorption of Ni(II), Cr(III) and Co(II) by cocoyam leaf under various conditions. The pH has much effect on the biosorption of these metal ions from aqueous solutions. The rate of the biosorption of these metal ions followed pseudo-second-order kinetics. The sorption isotherms of these metal ions onto the biosorbent are well described by the Freundlich isotherm model. The thermodynamic study shows that the biosorption of each of Ni(II), Cr(III) and Co(II) was spontaneous.

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SUGGESTED CITATION

Babarinde, A., J.O. Babalola, J. Adegoke, A.O. Osundeko, T.J. Ibadapo, C.A. Nwabugwu, and O.F. Ogundimu. 2012. "Biosorption of Ni(II), Cr(III), and Co(II) from Aqueous Solutions using Cocoyam (*Colocasia esculenta*) Leaf: Kinetic, Equilibrium, and Thermodynamic Studies". *Pacific Journal of Science and Technology*. 13(2):272-282.

