

Kinetic and Thermodynamic Parameters for the Biosorption of Ni(II), Cr(III), and Co(II) from Solutions using Cocoa (*Theobroma cacao*) Leaf.

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ABSTRACT

The use of cocoa leaf for the removal of Ni(II), Cr(III), and Co(II) from aqueous solution was investigated in this study with respect to adsorption capacity, kinetic, and thermodynamic studies. Adsorption capacity was rapid as appreciable level of metal ions uptake was achieved in the order Ni(II)>Cr(III)>Co(II). Results further showed maximum adsorption capacity of the adsorbents as 67.89mg g⁻¹ (Ni(II)), 59.35 mg g⁻¹ (Cr(III)) and 48.69 mg g⁻¹ (Co(II)) by cocoa leaf. Pseudo second-order kinetic model favored the adsorption process with R² ≈ 1 thus giving a better fit than any of the other three kinetic model tested, the rate of biosorption is of the order Co(II)>Ni(II)>Cr(III). Thermodynamic parameters calculated give positive enthalpy and entropy values in the order Cr(III)>Ni(II)>Co(II).

(Keywords: cocoa leaf, nickel, chromium, cobalt, biosorption)

INTRODUCTION

Toxic metal contamination of the environment from industrial effluents is a common problem worldwide due to various industrial operations. When they accumulate in the environment and in food chains, they can cause health problem to living organisms. The toxic nature of these pollutants has caused increased concern for their removal from industrial effluents.

Several conventional methods that have been employed in their removal have shown one demerit or the other. 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. Different biological materials 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. (Abia *et al.*, 2003; Horsfall *et al.*, 2003; Akar *et al.*, 2006; Bueno *et al.*, 2008; Babarinde *et al.*, 2009, 2010, 2012a-c).

Cocoa (*Theobroma cacao*) is a plant species from the family of Sterculiaceae, the fruit from which cocoa solids and cocoa butter are extracted are the basis of chocolate, as well as many Mesoamerican foods such as mole sauce. Cocoa pod has been used both in the natural and modified forms for the biosorption of different metal ions and dyes from solution (Bello *et al.*, 2011; Odoemelam *et al.*, 2011; Njoku *et al.*, 2011, 2012; Sonde and Odoemelam, 2012). However, the leaf of cocoa is unutilized thereby becoming 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

Cocoa (*Theobroma cacao*) leaves were harvested from a farm near 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. Thermostated Water bath 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.

Biosorption Studies

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 cocoa leaf with 25ml of 100 mg L^{-1} metal ion solution in a boiling tube within the range pH 1-6. 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.

The biosorption of the metal ions by cocoa (*Theobroma cacao*) leaf was studied at various time intervals (0-300 min) and at the concentration of 100 mg L^{-1} . This was done by weighing 0.5g of cocoa (*Theobroma cacao*) 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.

Batch biosorption study of metal ion was carried out using a concentration range of $10\text{-}300\text{ mg L}^{-1}$. This was done by introducing 0.5 g of the Cocoa (*Theobroma Cacao*) leaf into each of the boiling tubes employed and 25 ml of 100 mg L^{-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 25°C . The metal bound cocoa (*Theobroma cacao*) leaf was removed from the solution and the concentration of residual metal ion in each solution was determined.

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 0.5g of cocoa leaf with 25ml of 100 mg L^{-1} of metal ion solution at the optimal pH.

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

RESULTS AND DISCUSSION

FT-IR Characterisation of the Free and Metal-Bound Cocoa (*Theobroma cacao*) Leaf

The FT-IR spectra of dried unloaded, Ni-loaded, Cr-loaded and Co-loaded Cocoa (*Theobroma cacao*) leaf were taken to obtain information on the nature of possible interactions between the functional groups of Cocoa leaf biomass and the metal ions as presented in Figure 1. The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the functional groups such as -OH and C=O groups with lone pairs of electrons as shown in Figure 1.

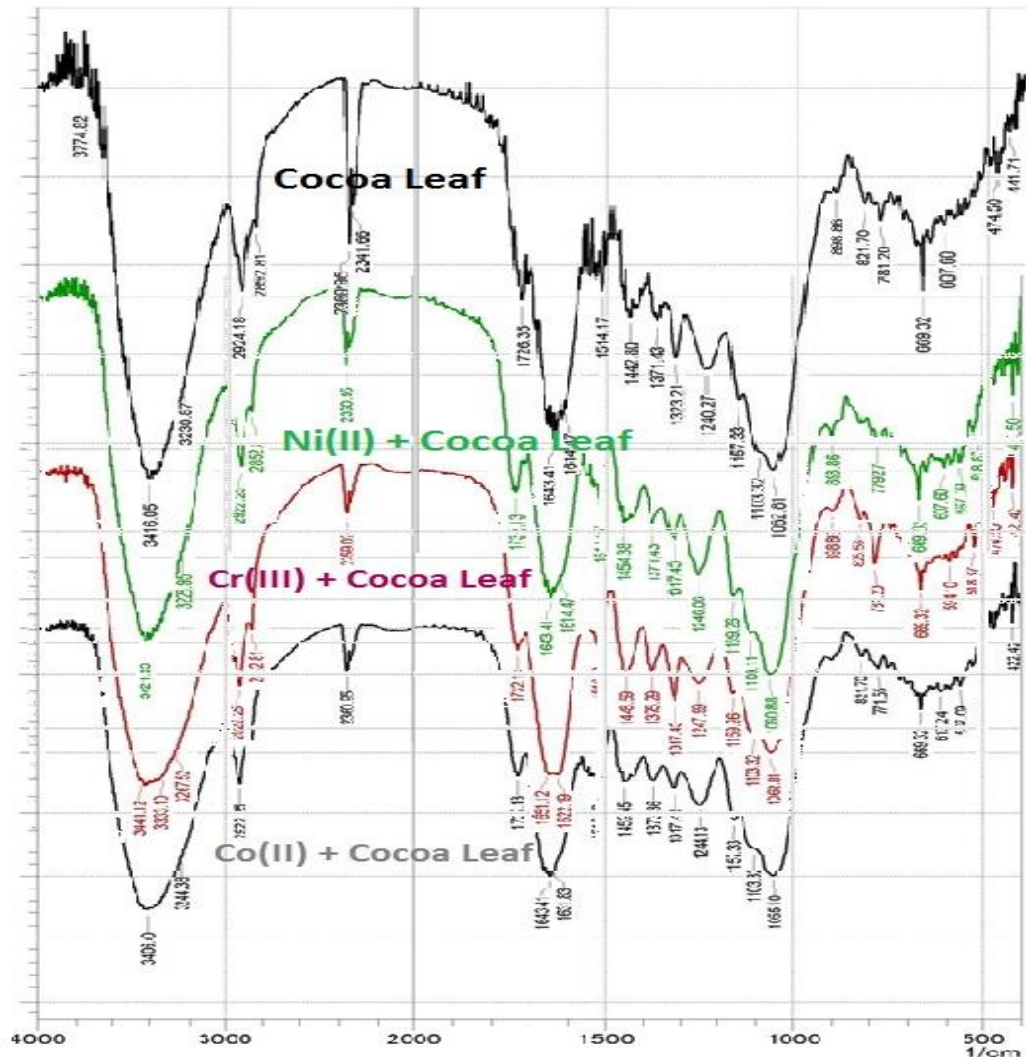


Figure 1: FTIR Spectra of the Free and Metal-Bound *Theobroma cacao* Leaf.

These bands are due to the functional groups of Cocoa 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 Cocoa (*Theobroma cacao*) 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 *et al.*, 2010; Pradhan *et al.*, 2007; Bueno *et al.*, 2008; Sun *et al.*, 2008; Ertugay and Bayhan, 2008). This implies that these functional groups would serve in the removal of positively charged ions from solution.

Table 1: FT-IR Spectra Characteristics of Cocoa (*Theobroma cacao*) Leaf before and after Biosorption of Ni(II), Cr(III), and Co(II) for 2 hours.

Metal ion	Absorption bands (cm ⁻¹)			Assignment
	Before	After	Difference	
Ni(II)	474.5	420.5	-54.0	-CN stretching
Cr(III)	474.5	422.42	-52.08	-CN stretching
Co(II)	474.5	422.42	-52.08	-CN stretching
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Ni(II)	1240.27	1246.06	5.79	C-O (medium weak) band
Cr(III)	1240.27	1247.99	7.72	C-O (medium weak) band
Co(II)	1240.27	1244.13	3.86	C-O (medium weak) band
Ni(II)	1614.47	1643.41	28.94	C=O stretching
Cr(III)	1614.47	1622.19	7.72	C=O stretching
Co(II)	1614.47	1631.83	17.36	C=O stretching
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Ni(II)	3416.05	3421.83	5.78	Bonded -NH,O-H Stretching
Cr(III)	3416.05	3441.12	5.07	Bonded -NH,O-H Stretching
Co(II)	3416.05	3406.4	-9.65	Bonded -NH,O-H Stretching

Effect of Solution pH on Metal ion Biosorption

The pH of solution has been established to be a vital parameter in biosorption process (Babarinde, 2012a-c; Sun *et al.*, 2008). 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 Cocoa (*Theobroma Cacao*) 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 from the liquid phase to the solid phase, the biosorbent with lone pair of electrons, and can be considered as a reversible reaction with an equilibrium being made between the two ions in solution.

Biosorption Kinetics

Figure 3 illustrates the dynamic biosorption process of the three metal ions on Cocoa (*Theobroma cacao*) leaf. It is observed that the biosorptive quantities of the three metal ions on Cocoa (*Theobroma cacao*) leaf increased 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).

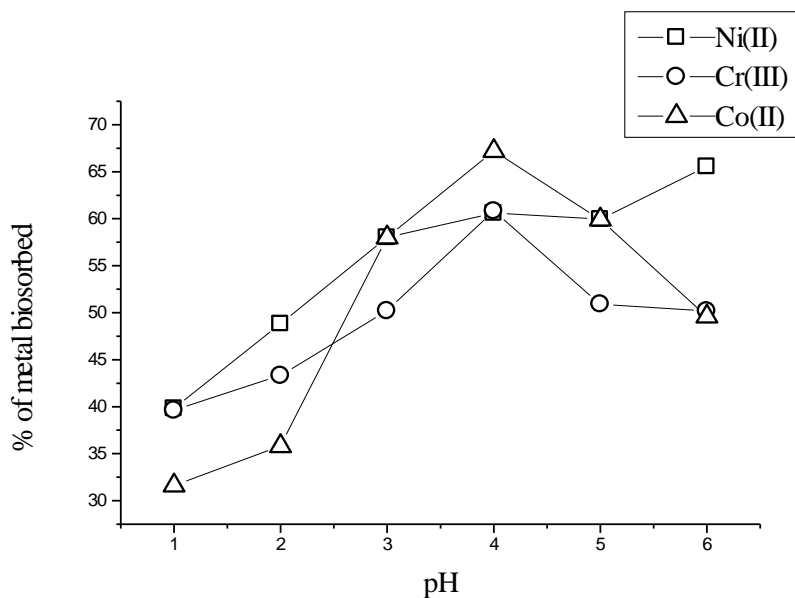


Figure 2: pH-Dependent Profile for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa (*Theobroma cacao*) Leaf at 25°C.

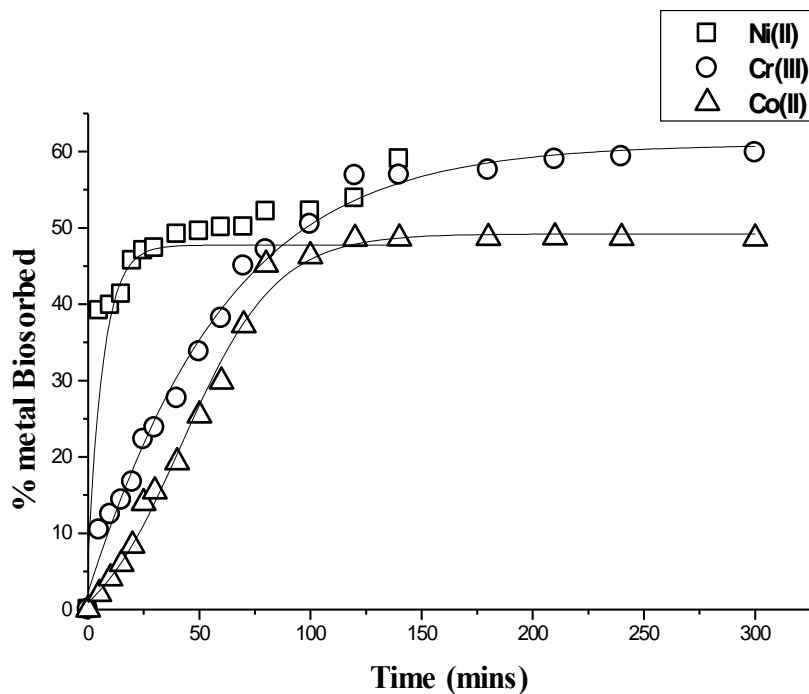


Figure 3: Time Course for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa Leaf at 25°C.

In order to investigate the kinetics of the biosorption of these metal ions on Cocoa (*Theobroma Cacao*) leaf, four kinetic models were employed. These are the pseudo-first-order, the pseudo-second-order, the Elovich and the intra-particle 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):

$$\text{rate} = -\frac{d[A]}{dt} = k [A]^n \quad (1)$$

Which can also be written as:

$$\frac{d}{dt} q_t = k_1 (q_e - q_t) \quad (2)$$

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

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

This can be rearranged to obtain a linear form:

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

Where k_1 is the Lagergren rate constant of the biosorption (min^{-1}); q_e and q_t are the amounts of metal ions biosorbed (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:

$$\frac{d}{dt} q_t = k_2 (q_e - q_t)^2 \quad (5)$$

On integrating between boundary conditions, we have:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

On rearrangement, we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

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 concentrations of the three metal ions as presented in Figure 4.

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

$$q_t = A + B \ln t \quad (8)$$

The intra-particle diffusion equation given as:

$$R = K_s t^b \quad (9)$$

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

$$\log R = b \log t + \log K_s \quad (10)$$

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.

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 Cocoa (*Theobroma Cacao*) leaf.

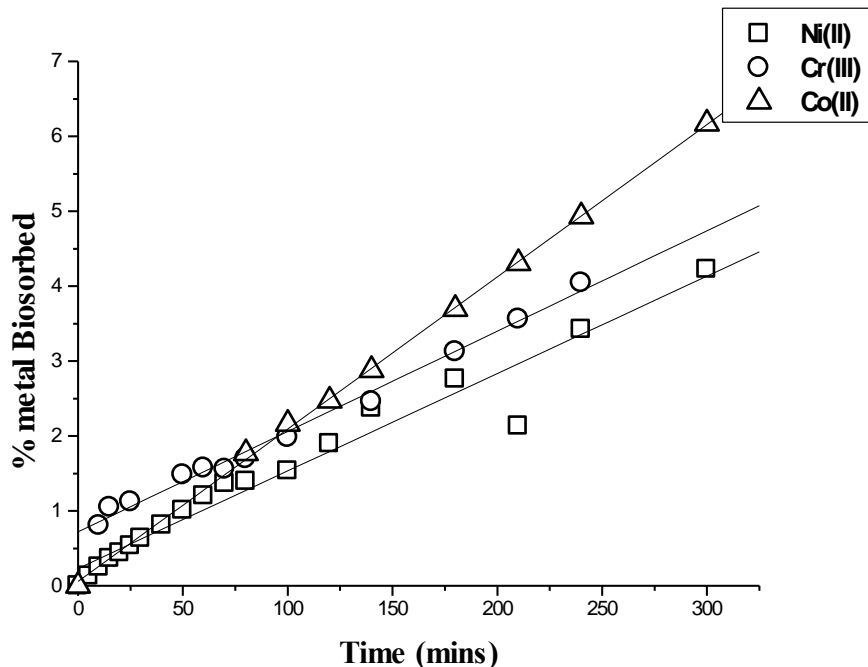


Figure 4: The Pseudo-Second-Order Kinetic Plot for the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa (*Theobroma cacao*) Leaf at 25°C.

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

Metal Ion	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e(\text{mg g}^{-1})$	R^2	S.D.
Ni(II)	1.3109×10^{-3}	67.89	0.98808	0.10514
Cr(III)	3.9400×10^{-4}	59.35	0.99251	0.09447
Co(II)	1.362×10^{-2}	48.69	0.99964	0.03913

The result shows that the rate of biosorption of the metal ions is of the order $\text{Co(II)} > \text{Ni(II)} > \text{Cr(III)}$ 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 $\text{Ni(II)} > \text{Cr(III)} > \text{Co(II)}$. This implies that the amount of each metal biosorbed depends on its valency.

Biosorption Efficiency

The result of the study on the effect of initial metal ion concentration on biosorption efficiency is shown in Figure 5.

The plots show that the biosorption efficiency of the biomass increased with increase in the initial metal ion concentration for all the metal ions which might be due to increase in effective collision between the metal ions and the active sites. The biosorption efficiency (E) for each metal ion was calculated as:

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \quad (11)$$

Where C_i and C_e are the initial and the equilibrium metal ion concentrations (mg L^{-1}), respectively.

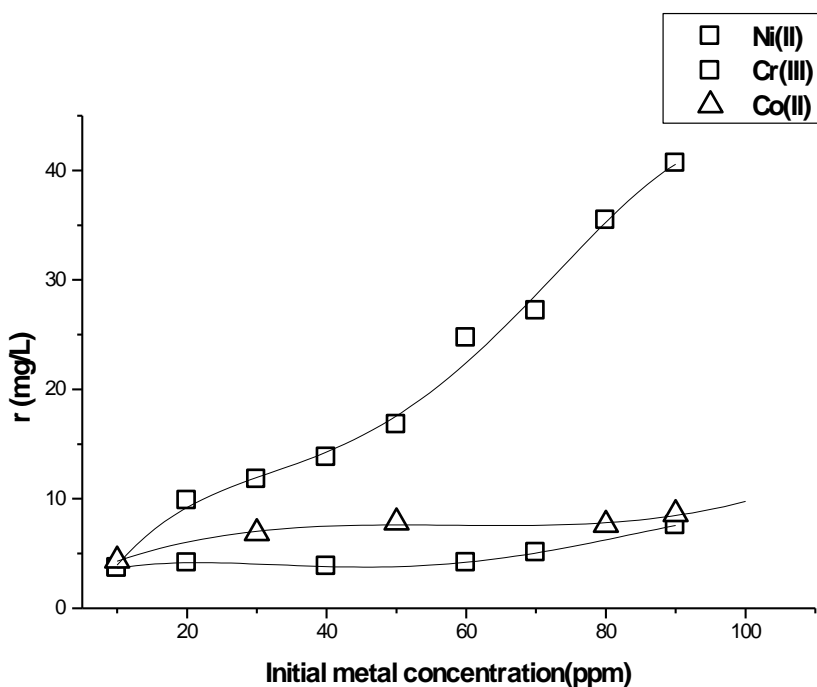


Figure 5: Effect of Initial Concentration on Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa at 25°C.

Effect of Biomass Dosage on Biosorption

The effect of biomass dosage on biosorption efficiency is reported in Figure 6. 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 (Babarinde *et al.*, 2009; 2012a-c).

Biosorption Thermodynamics

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 (Sun *et al.*, 2008; de la Rosa *et al.*, 2008).

$$\Delta G^\circ = -RT \ln K_c \quad (12)$$

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

$$K_c = \frac{C_{ad}}{C_e} \quad (13)$$

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 behaviour of the biosorption of Ni(II), Cr(III) and Co(II) onto Cocoa (*Theobroma cacao*) 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). The change in free energy is related to other thermodynamic properties as:

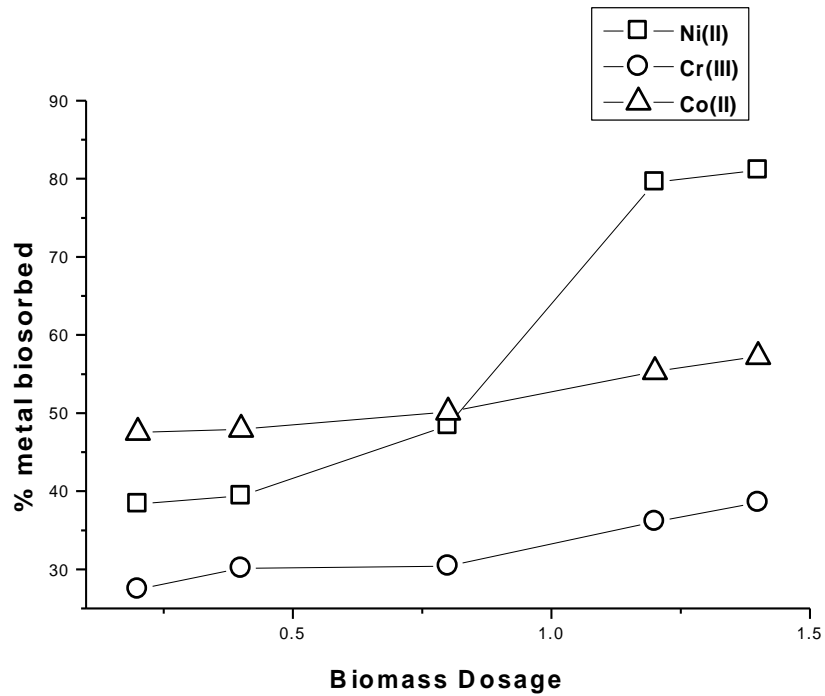


Figure 6: Effect of Biomass Dosage on the Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa (*Theobroma cacao*) Leaf at 25°C.

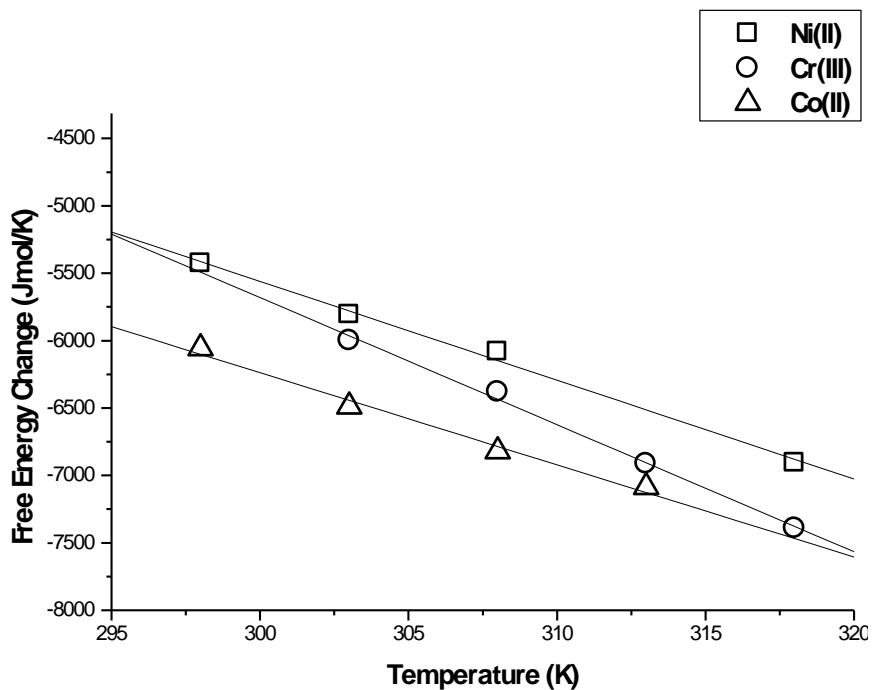


Figure 7: Thermodynamic Plots for Biosorption of Ni(II), Cr(III), and Co(II) by Cocoa Leaf at 25°C.

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

Metal ion	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	A (kJmol ⁻¹) @303 K	A (kJmol ⁻¹) @ 313 K
Ni(II)	16.439	73.3296	18.96	19.04
Cr(III)	22.592	94.2454	25.11	25.19
Co(II)	14.267	68.3508	16.79	16.87

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

Where T is the absolute temperature (K); R is the gas constant (8.314 Jmol⁻¹.K⁻¹). ΔH° (J.mol⁻¹) and ΔS° (J.mol⁻¹.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 7 are linear over the entire range of temperature investigated.

The negative values of ΔG° indicate spontaneity of each biosorption process, with the order of spontaneity being Co(II)>Cr(III)>Ni(II). The positive value of ΔH° indicates the presence of an energy barrier in the biosorption process. Similarly, the ΔS° values for the three metal ions are positive indicating increase in randomness during the biosorption process for the metal ions. These positive values of ΔS° observed for the biosorption of these metal ions indicate an increase in randomness at the solid/solution interface during their biosorption.

The order of increasing disorder being Co(II)<Ni(II)<Cr(III). It has been reported that the change of standard free energy for physisorption is in the range of -20 to 0 kJ mol⁻¹ and for chemisorption varies between -80 and -400 kJmol⁻¹ (Vimonses *et al.*, 2009; Sen *et al.*, 2011). In the present study, the overall ΔG° has values ranging from -7.5 to -5.25 kJ mol⁻¹. These results correspond to a spontaneous physical adsorption of the metal ions, indicating that this system does not gain energy from external resource (Vimonses *et al.*, 2009; Arias and Sen 2009).

The decrease in ΔG° with increase in temperature indicates more efficient biosorption at higher

temperature. This is also supported by the increase in the value of biosorption capacity of the biosorbent with rise in temperature. Furthermore, the magnitude of activation energy (A) gives an idea about the type of adsorption which is mainly diffusion controlled process (not diffusivity of solute through micropore wall surface of a particle) or chemical reaction processes (Abd El-Latif *et al.*, 2010). Energies of activation, A, below 42 kJ/mol indicate diffusion-controlled processes, and higher values give chemical reaction-based processes. Therefore, energy of activation, A, has been calculated as per the following relation:

$$A = \Delta H^\circ + RT \quad (16)$$

The values of A at two different temperatures have been tabulated in Table 4. In this study, the activation energy (A) values were less than 42 kJmol⁻¹ indicating diffusion-controlled adsorption processes.

CONCLUSION

In this work we have studied the biosorption of Ni(II), Cr(III) and Co(II) by cocoa (*Theobroma cacao*) leaf under various physicochemical conditions. The pH significantly effects the level of biosorption of these metal ions from aqueous solutions. The rate of the biosorption of these metal ions followed pseudo-second-order kinetics. The thermodynamic study shows that the biosorption of each of Ni(II), Cr(III) and Co(II) was spontaneous. This study shows that cocoa leaf has high potential for treating industrial effluents containing Ni(II), Cr(III), and Co(II).

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