

# Kinetic and thermodynamic studies of the biosorption of Ni(II), Cr(III) and Co(II) from solutions onto Kolanut (*Cola acuminata*) leaf

N. A. Adesola Babarinde<sup>1\*</sup>, J. Oyebamiji Babalola<sup>2</sup>, Fatihu A. Omoiya<sup>1</sup>, Nurudeen A. Odufuwa<sup>1</sup> and Oluwatobi V. Omotade<sup>1</sup>

<sup>1</sup>Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye, Nigeria

<sup>2</sup>Department of Chemistry, University of Ibadan, Ibadan, Nigeria

## Abstract

Kolanut (*Cola acuminata*) leaf was investigated for its potential in the biosorption Ni(II), Cr(III) and Co(II) from solutions under various physicochemical parameters such as pH, time, concentration, and temperature. The FTIR spectral characteristics of Kolanut leaf showed the presence of ionizable groups that could participate in the binding of the metal ions in solution. The kinetic studies showed that biosorption process was best represented by pseudo-second-order kinetics among four kinetic models tested. Among Freundlich and Langmuir adsorption isotherms, results shows that Freundlich isotherm better represents the equilibrium data for Ni(II) and Co(II) while Langmuir isotherm better represents the equilibrium data for Cr(III). The study on the effect of biomass dosage indicates that the dosage of the biomass significantly affected the uptake of the metal ions from solution. Thermodynamic parameters such as free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and the activation energy (A) were determined. The order of spontaneity was found to be Co(II)>Cr(III)>Ni(II). The activation energy for each of the metal ions was less than  $42\text{kJmol}^{-1}$  at 303K which suggests that each was a diffusion controlled process.

**Key words:** Biosorption, Co(II), Cr(III), Ni(II), isotherm, kinetics, thermodynamics

**Full length article** Received: 21-05-2013 Revised: 08-07-2013  
\*Corresponding Author, e-mail: solababarinde@yahoo.com

Accepted: 14-07-2013 Available online: 31-07-2013  
Tel: +234-8037232934

## 1. Introduction

Heavy metals are major pollutants in the environment due to increased industrialisation worldwide. The environmental pollution that accompanies industrialisation is a serious menace that must be given serious attention. Particularly, the effect of the toxic metal ions in industrial effluents which enter the food chain and cause damage to plants and animals lives. The danger they pose to plants and animals in the environment calls for an effective, efficient and economical means of mitigating their levels before they are discharged into the environment. Biosorption has proved to be an efficient and cost effective means of regulating the effect of these pollutants. It is cheaper than the conventional methods which are rather expensive and often time have some other environmental effects. Biosorption of various metal ions has been carried out on various agricultural wastes in order to determine the feasibility and effectiveness of their application to the treatment of industrial effluents containing metal ions [1-9]. Kolanut (*Cola acuminata*) belongs to the family malvaceae and genus Cola. It is similar to *Cola nitida* but with narrower leaves. *Cola acuminata* is an evergreen tree of about 20meters in height, and has long ovoid leaves pointed

at both ends with a leathery texture. The fruits of the tree are grossly consumed in its raw form, or as flavourers in drinks due to their caffeine content. The leaves are usually unutilized thereby constituting environmental nuisance. It was for this reason that this readily available agricultural waste was investigated for its potential in treating industrial effluents containing Ni(II), Cr(III) and Co(II).

## 2. Materials and methods

### 2.1. Biomass preparation

Kolanut leaves were harvested 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.

### 2.2. 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

CoSO<sub>4</sub>·7H<sub>2</sub>O, respectively, using distilled water. The test solutions with different concentrations of Ni(II), Cr(III) and Co(II) were prepared using appropriate subsequent dilution of the stock solution. The range of concentrations of Ni(II), Cr(III) and Co(II) prepared from standard solution varies between 10 and 100 mgL<sup>-1</sup>. The initial pH of the solution was adjusted accordingly with a pH meter. Before mixing the biosorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl and 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 400-4000 cm<sup>-1</sup> using a Shimadzu FT-IR model 8400S spectrophotometer.

### 2.3. Batch biosorption study

The biosorption study was carried out by contacting 0.5g of the Kolanut 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 25°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.

### 2.4. 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 Kolanut leaf with 25ml of 100 mgL<sup>-1</sup> metal ion solution in a boiling tube within the range pH 1- 6 to avoid precipitation at higher pH values. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1M HCl and/or 0.1M NaOH. The boiling tubes containing the mixture were left in a water bath for 4 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.

### 2.5. Effect of contact time on biosorption

The biosorption of the metal ions by Kolanut leaf was studied at various time intervals (0-300 min) and at the concentration of 100 mg L<sup>-1</sup>. This was done by weighing 0.5g of Kolanut leaf into each boiling tube and 25ml of 100 mg L<sup>-1</sup> 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.

### 2.6. Effect of initial metal ion concentration on biosorption

Batch biosorption study of metal ion was carried out using a concentration range of 10 -100 mgL<sup>-1</sup>. This was

done by introducing 0.5 g of the Kolanut leaf into each of the boiling tubes employed and 25 ml of 100 mgL<sup>-1</sup> 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 Kolanut leaf was removed from the solution and the concentration of residual metal ion in each solution was determined.

### 2.7. Effect of temperature on biosorption

The batch biosorption process was studied at different temperatures of 20 - 50°C in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.5 g of Kolanut leaf with 25ml of 100 mgL<sup>-1</sup> of metal ion solution at the optimal pH at the different temperature investigated.

### 2.8. Statistical analyses

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

## 3. Results and Discussion

### 3.1. FT-IR studies of the free and metal-bound Kolanut leaf

The FT-IR spectra of dried unloaded, Ni-loaded, Cr-loaded and Co-loaded Kolanut leaf were taken to obtain information on the nature of possible interactions between the functional groups of Kolanut leaf biomass and the metal ions as presented in Fig. 1. The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the functional groups such as N=O, -OH and C=O groups as shown in Figure 1. These bands are due to the functional groups of Kolanut leaf that participated 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 Kolanut 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 which are able to interact with cations [1, 10 -13]. This implies that these functional groups would serve in the removal of positively charged ions from solution.

### 3.2. Effect of solution pH on metal ion biosorption

The pH control in the system is important because it affects both the configuration of the active ion-exchange sites as well as the ionic states of the sorbate in the solution [14]. The pH of solution plays a vital role in the biosorption of the metal ions. It is an important parameter governing the uptake of heavy metals by biosorption processes. Not only does it affect metal species in solution, but also influences the surface properties of biosorbents in terms of dissociation of binding sites and surfaces. (As 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.

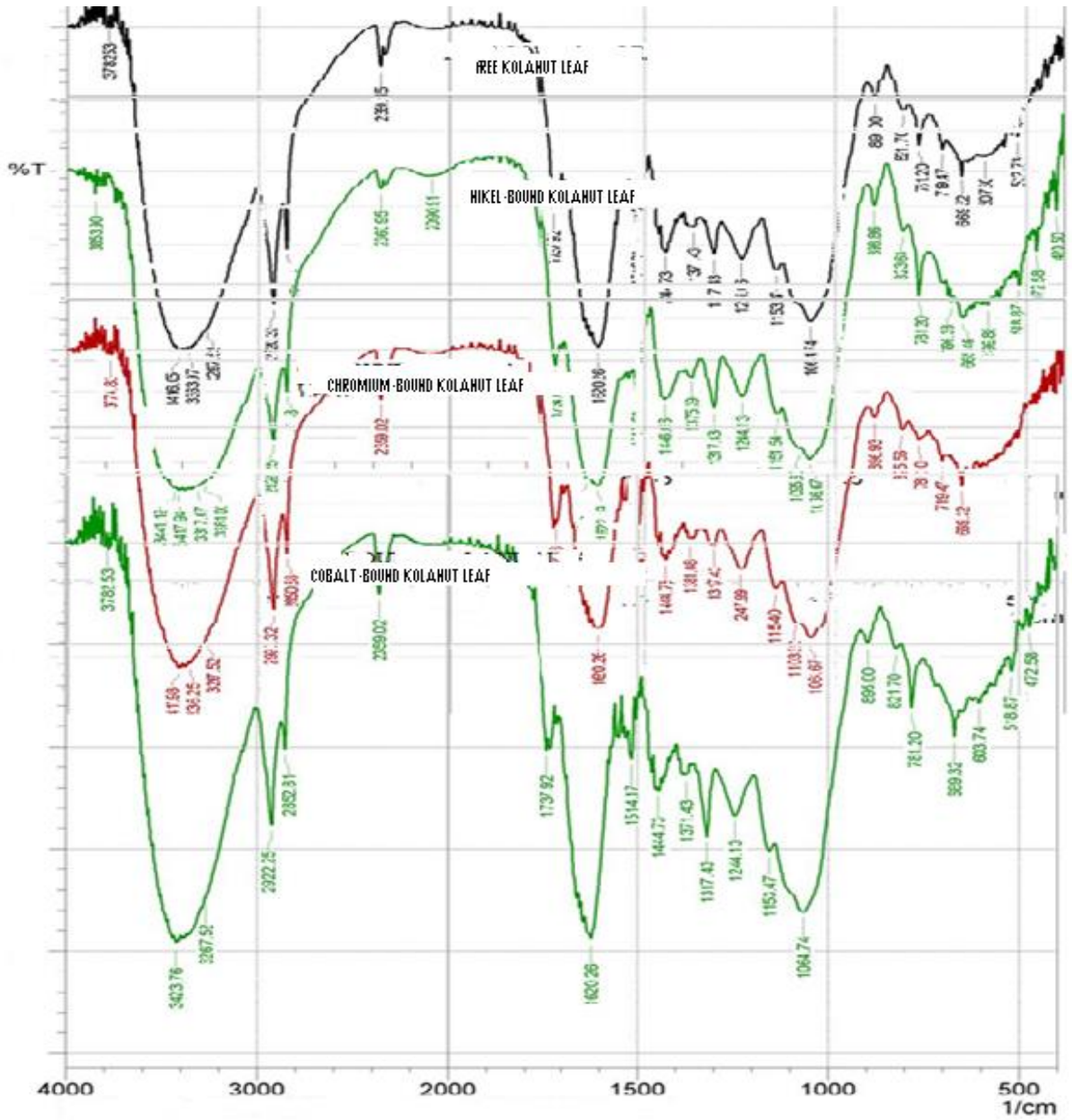


Fig. 1. FT-IR spectra of the free and metal-bound Kolanut (*Cola acuminata*) leaf

**Table 1:** FT-IR Spectra characteristics of Kolanut (*Cola acuminata*) leaf before and after biosorption of Ni(II), Cr(III) and Co(II) for 2 hours.

Metal ion	Absorption bands( $\text{cm}^{-1}$ )			Assignment
	Before	After	Difference	
Ni(II)		3441.12	-25.07	N-H-stretching & bonded OH
Cr(III)	3416.05	3417.98	-1.93	
Co(II)		3423.26	-7.21	
Ni(II)		1622.19	-1.93	C=O stretching
Cr(III)		1620.26	0	
Co(II)	1620.26	1620.26	0	
Ni(II)		1066.67	-1.93	-C-O,- -C-N
Cr(III)		1066.67	-1.93	
Co(II)	1064.74	1064.74	0	

**Table :** Parameters of the pseudo-second-order kinetic model for the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut (*Cola acuminata*) leaf.

Metal ion	$k_2$ ( $\text{g.mg}^{-1} \text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$
Ni(II)	$4.91 \times 10^{-2}$	51.89	0.9776
Cr(III)	$4.86 \times 10^{-5}$	119.76	0.9954
Co(II)	$7.80 \times 10^{-4}$	71.02	0.9991

**Table 3:** Freundlich and Langmuir isothermal parameters for the biosorption of Ni(II), Cr(III) and Co(III) onto Kolanut (*Cola acuminata*) leaf

Metal ion	Freundlich parameters				Langmuir parameters for Cr(III)			
	n	$K_f$	$R^2$	S.D.	$b_m$	$\Gamma_m$	R	S.D
Ni(II)	1.5569	1.3773	0.9728	0.0277	6.1989	34.6021	0.99454	0.01044
Co(II)	1.3511	0.2926	0.9968	0.0157				

**Table 4:** Thermodynamic parameters for the biosorption of Ni(II), Cr(III) and Co(II) onto Kolanut (*Cola acuminata*) leaf

Metal ion	$\Delta H^\circ$ ( $\text{kJmol}^{-1}$ )	$\Delta S^\circ$ ( $\text{JmolK}^{-1}$ )	A ( $\text{Jmol}^{-1}$ ) @ 298 K	A ( $\text{Jmol}^{-1}$ ) @ 303K
Ni(II)	-2.07	53.52178	-2.63	-2.64
Cr(III)	7.21	38.45298	9690.2721	9.73
Co(II)	8.52	45.0676	11041.8921	11.04

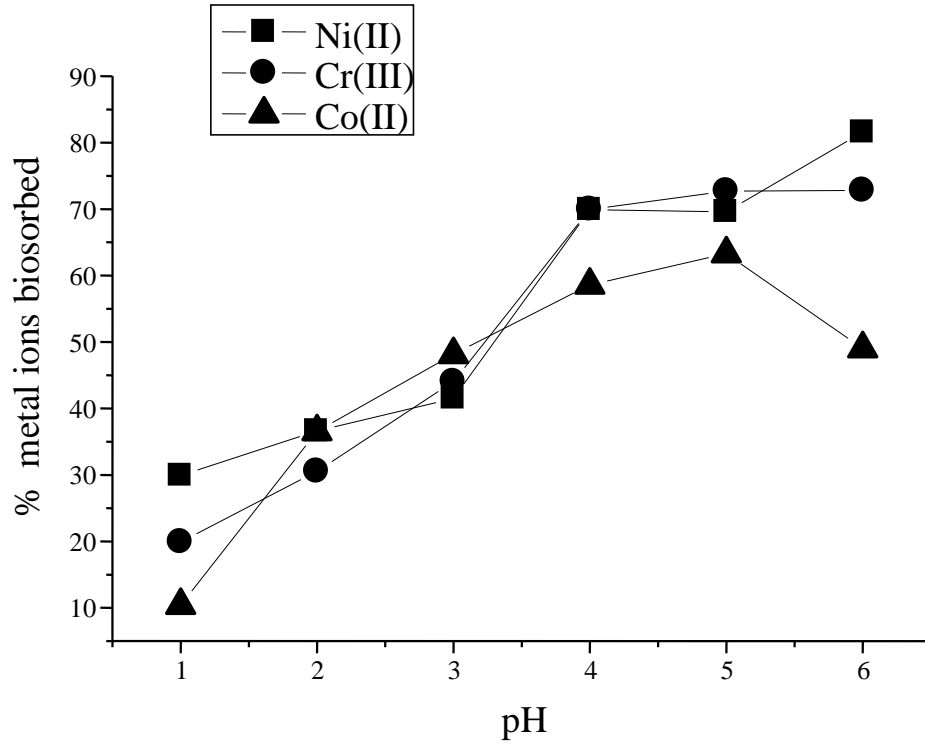


Fig. 2. pH-dependent profile of the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut leaf.

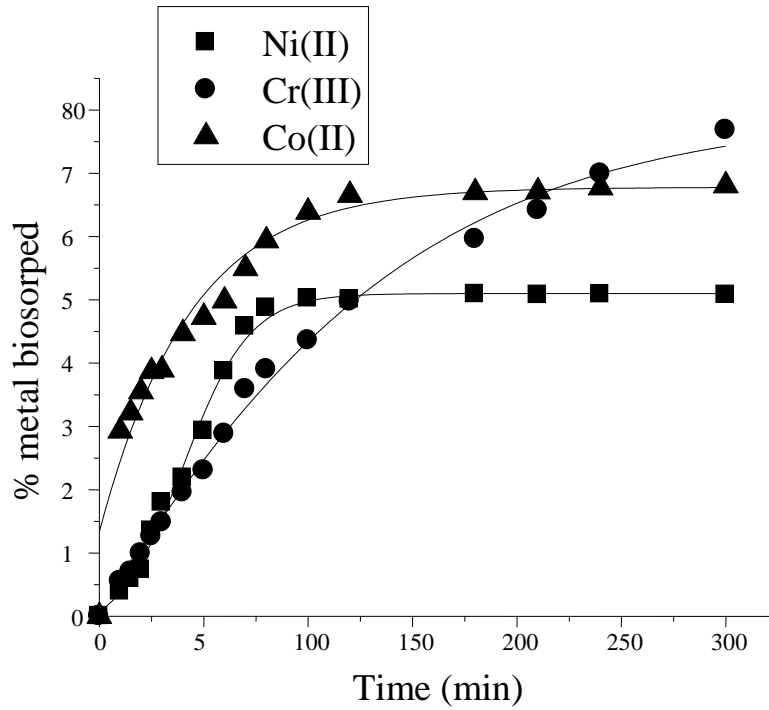
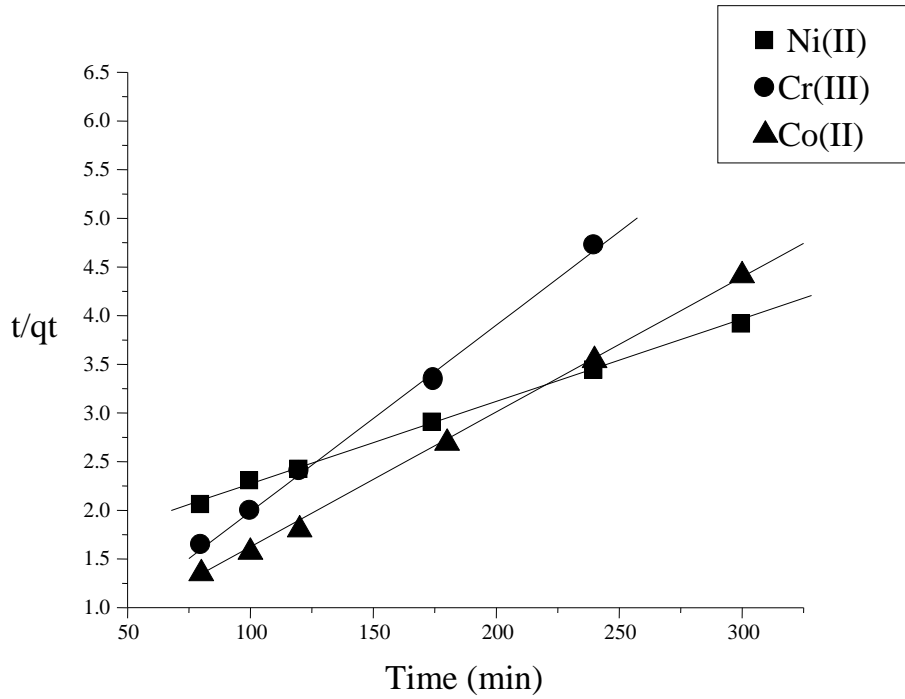
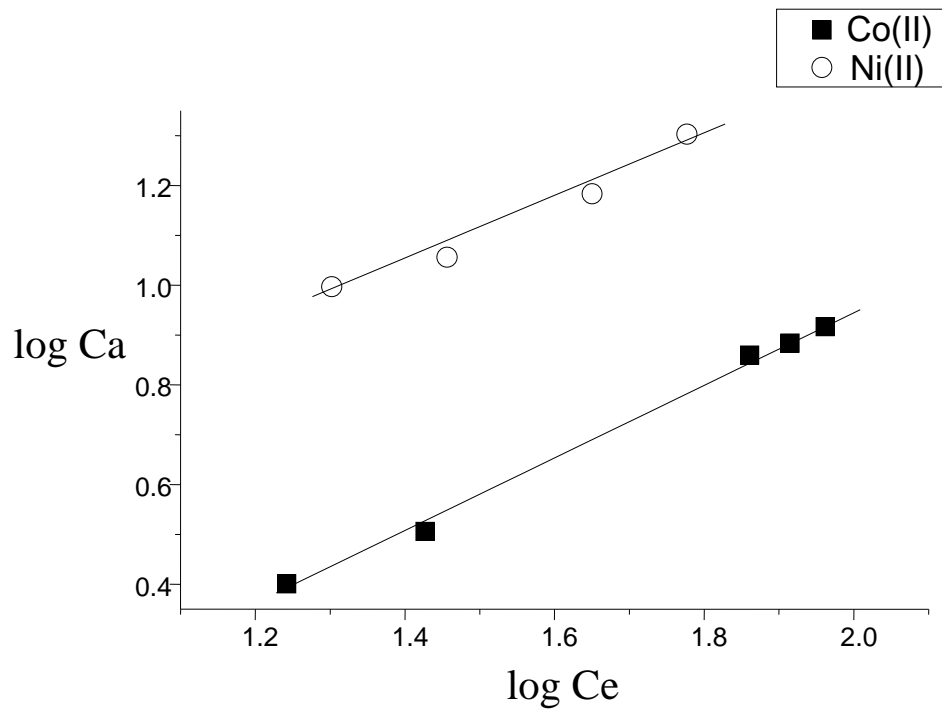


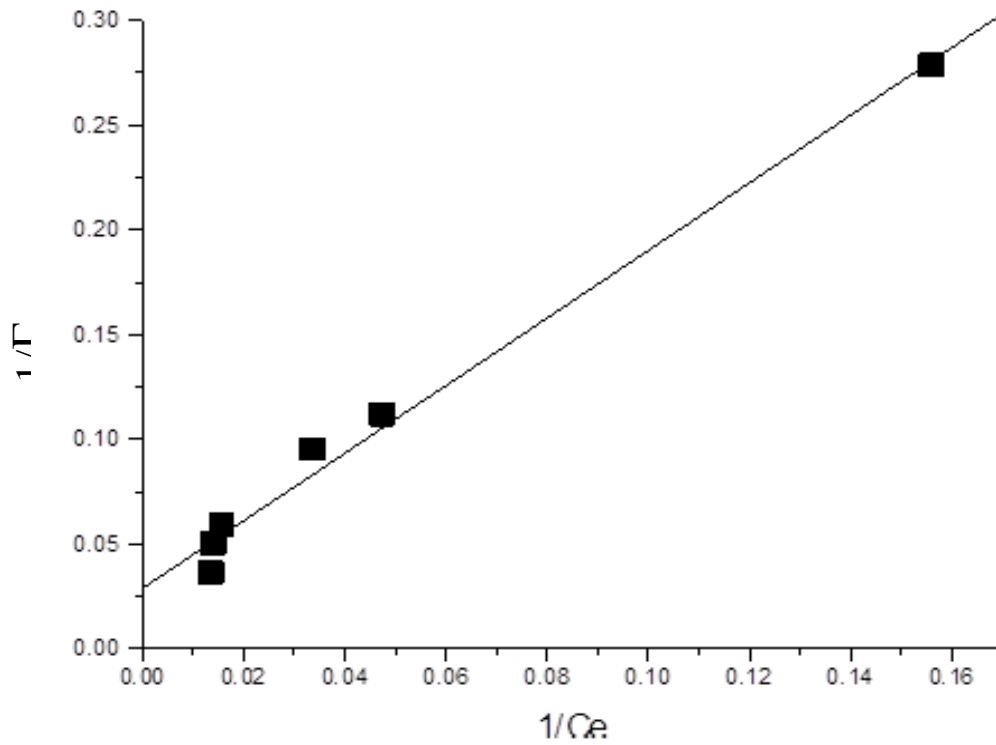
Fig. 3. Time course of the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut leaf.



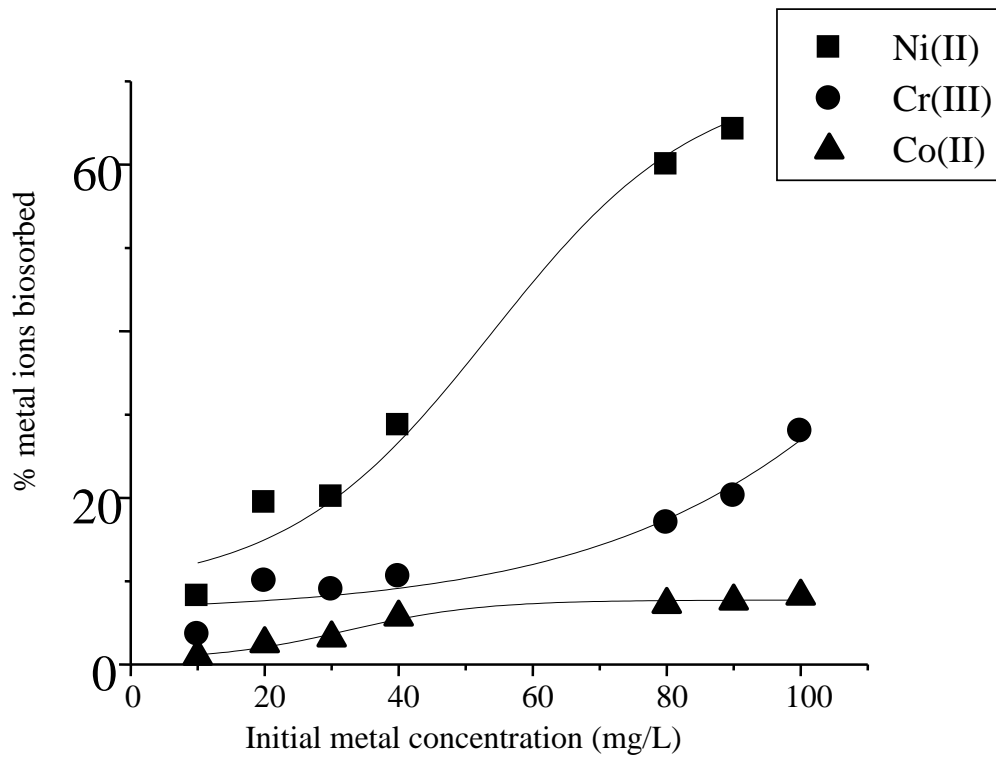
**Fig. 4.** The pseudo-second-order kinetic plot for the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut (*Cola acuminata*) leaf at 25°C.



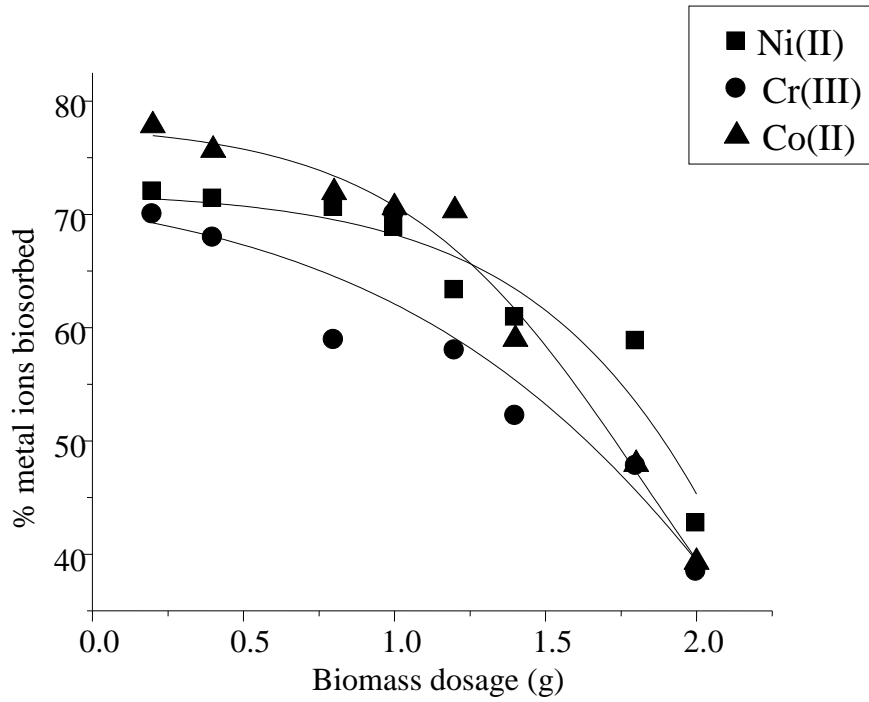
**Fig. 5a.** Freundlich isotherm for the biosorption of Ni(II) and Co(II) onto Kolanut leaf



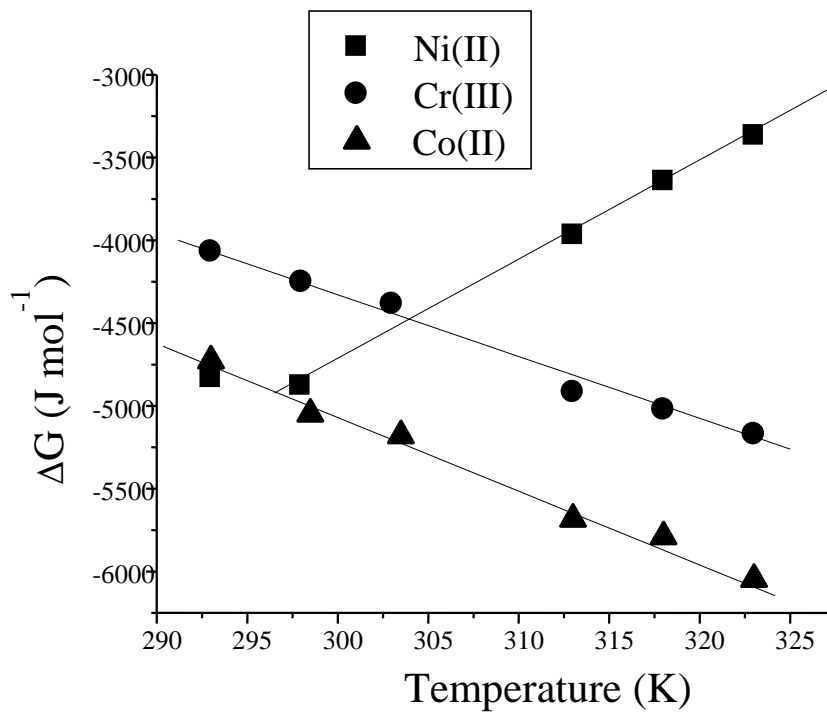
**Fig. 5b.** Langmuir Isotherm for the biosorption of Cr(III) from Solution onto Kolanut leaf at 25°C and pH6.



**Fig. 6.** Effect of initial metal ion concentration on the biosorption of Ni(II), Cr(III) and Co(II) onto Kolanut (*Cola acuminata*) leaf



**Fig.7.** Effect of dosage on the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut (*Cola acuminata*) leaf



**Fig. 8.** Thermodynamic plots for the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut (*Cola acuminata*) leaf



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 Kolanut leaf at various solution pH values. In each case, the biosorption increased steadily as the pH increased from pH 1 to pH 5. It could also be deduced that biosorption of Ni(II) and Cr(III) on *Cola acuminata* are best at pH 6 and Co(II), best at pH 5. 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:



### 3.3. Biosorption kinetics

A plot of the contact time against the percentage of metal ion biosorbed describes the dynamic biosorption process of the three metal ions on Kolanut leaf as reported in Figure 3. It is observed that the biosorptive quantities of the three metal ions on Kolanut 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, for two of the metal ions (Ni and Co), 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 [9]. The biosorption of Ni(II) and Co(II) achieves equilibrium within 3 hr although the rate of uptake of the three metal atoms are different. This might be due to the differences in hydrated ionic sizes of the metal ions [15]. The third metal seem not to have achieved equilibrium till the end of the 5 h considered.

In order to investigate the kinetics of the biosorption of these metal ions Kolanut 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 [13]

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

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 ( $\text{min}^{-1}$ );  $q_e$  and  $q_t$  are the amounts of metal ions sorbed ( $\text{mg g}^{-1}$ ) 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  $100 \text{ mg L}^{-1}$  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 concentrations of the three metal ions as presented in Figure 3. The data were equally subjected to the Elovish 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  $R^2 \geq 0.98$  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 Kolanut (*Cola acuminata*) leaf. 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

[15]. The pseudo-second-order rate constants obtained indicate that the rate of biosorption is of the order Ni(II)>Co(II)>Cr(III) while the order of biosorption capacity is Cr(III)>Co(II)>Ni(II). The differences observed could be accounted for in terms of differences in ionic charges, chemical affinity, ion exchange capacity and the hydrated ionic sizes of the ions in solution [15].

### 3.4. Biosorption isotherm

Figure 5 illustrates the biosorption isotherm of Ni(II), Cr(III) and Co(II) on Kolanut (*Cola acuminata*) 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 heterogenous 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  $\Gamma$ ,  $\Gamma_m$  and  $b_m$  are the Langmuir parameters.

The equilibrium data for Ni(II) and Co(II) were better represented by Freundlich isotherm as presented in Figure 5a while the Cr(III) data were better represented by Langmuir isotherm as presented in Figure 5b. The resulting isothermal parameters are presented in Table 3

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.

### 3.5. 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 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

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

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

### 3.6. 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 [3-5].

### 3.7. 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 favoured by increase in temperature while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation [12]

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

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 ( $\text{mg L}^{-1}$ ) in solution and on biosorbent, respectively. Consequently, the thermodynamic behaviour of the biosorption of Ni(II), Cr(III) and Co(II) onto Kolanut (*Cola acuminata*) leaf was evaluated through the change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ). The thermodynamic parameters like enthalpy and entropy are obtained using van't Hoff equation [10, 16]. 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 ( $8.314 \text{ Jmol}^{-1} \cdot \text{K}^{-1}$ ).  $\Delta H^\circ$  and  $\Delta S^\circ$  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.

The negative values of  $\Delta G^\circ$  indicate spontaneity of each biosorption process, with the order of spontaneity being Co(II)>Cr(III)>Ni(II). The negative value of  $\Delta H^\circ$  for the biosorption of Ni(II) suggests exothermic nature of the biosorption processes while the positive value of those of Cr(III) and Co(II) suggests that the process is endothermic. This is also supported by the increase in the value of biosorption capacity of the biosorbent with rise in temperature. The positive value of  $\Delta H^\circ$  indicates the presence of an energy barrier in the biosorption process. Similarly, the  $\Delta S^\circ$  values for the Cr(III) and Co(II) are positive indicating increase in randomness during the biosorption process for the metal ions. These positive values of  $\Delta S^\circ$  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 Ni(II)>Co(II)>Cr(III).

Generally, the change of standard free energy for physisorption is in the range of  $-6$  to  $-3 \text{ kJ mol}^{-1}$  and for chemisorption varies between  $-80$  and  $-400 \text{ kJmol}^{-1}$  [17, 18]. In the present study, the overall  $\Delta G^\circ$  has values ranging

from  $-7.5$  to  $-2.0$  kJ mol<sup>-1</sup>. These results correspond to a spontaneous physical adsorption of the metal ions, indicating that this system does not gain energy from external resource [17, 19]. The decrease in  $\Delta G^\circ$  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 [20]. 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:

$$A = \Delta H^\circ + RT \quad (19)$$

The values of A at two different temperatures are presented in Table 4. In this study, the activation energy (A) values are less than 42 kJmol<sup>-1</sup> indicating diffusion-controlled adsorption processes.

#### 4. Conclusions

This work has investigated the biosorption of Ni(II), Cr(III) and Co(II) by Kolanut (*Cola acuminata*) leaf under various conditions. The results have shown that pH has much effect on the biosorption of these metal ions from aqueous solutions. The rate of the biosorption of these metal ions was best represented by the pseudo-second-order kinetics. The Freundlich isotherm better represents the equilibrium data for Ni(II) and Co(II) while Langmuir isotherm better represents the equilibrium data for Cr(III). The thermodynamic study shows that the biosorption of each of Ni(II), Cr(III) and Co(II) onto Kolanut (*Cola acuminata*) leaf was spontaneous. The study shows that Kolanut leaf has high potential to be used for treating industrial effluents containing Ni(II), Cr(III) and Co(II).

#### References

- [1] B.Y.O Bueno, M.L. Torem, F. Molina, and L.M.S. de Mesquita. (2008). Biosorption of lead(II), chromium (III) and copper (II) by *R. opacus*: Equilibrium and kinetic studies. *Mineral Engineering* 21 65-75.
- [2] Z. Chen, W. Ma and M. Han (2008). Biosorption of nickel and copper onto treated alga (*Undariapinnarlifida*): Application of isotherm and kinetic models. *Journal of Hazardous Materials* 155 (1-2): 327-333.
- [3] N.A.A Babarinde, J.O Babalola, A.O. Ogunfowokan and A.C.Onabanjo. (2009). Kinetic, equilibrium and thermodynamic studies of the biosorption of cadmium (II) from solution by *Stereophyllum radiculosum*. *Toxicological and Environmental Chemistry* 91(5) 911-922.
- [4] N.A.A Babarinde, J.O Babalola, J. Adegoke, O. Maranzu, T. Ogunbanwo and E. Ogunjinrin. (2012a). Kinetic, isothermal and thermodynamic studies of the biosorption of Ni(II) and Cr(III) from

aqueous solutions using banana (*Musa acuminata*) leaf. *International Journal of Physical Sciences* 7(9) 1376-1385.

- [5] N.A.A Babarinde, J.O Babalola, J. Adegoke, A. O. Osundeko, S. Olasehinde, A. Omodehin and E. Nurhe (2012b). Biosorption of Ni(II), Cr(III) and Co(II) from solutions using *Acalypha hispida* leaf: Kinetics, Equilibrium and Thermodynamics. *Journal of Chemistry* <http://dx.doi.org/10.1155/2013/460635>.
- [6] A. Babarinde, J.O Babalola, J. Ashidi; J. Adegoke, A. Osundeko, K. Ogundipe, A. Omojola and A. Obisanya. (2013). Batch equilibrium biosorption of Ni(II), Cr(III) and Co(II) from Solution using Bitter leaf (*Vernonia amygdalina*): kinetics, isotherm, and thermodynamics. *International Journal of Chemical and Biochemical Sciences*. 3(2013)101-109
- [7] A.Y. Okasha and H.G. Ibrahim. (2010). Removal of Cu<sup>2+</sup> ions from aqueous solutions by adsorption on Libyan soil. *Journal Environment Science and Engineering* 4(10) (35) 9 -15.
- [8] K. Vijayaraghavan and R. Balasubramanian. (2010). Single and binary biosorption of cerium and europium onto crab shell particles. *Chemical Engineering Journal* 163: 337 -343
- [9] Y. Wu, L. Zhang., C. Gao., X. Ma and R. Han. (2010). Adsorption of copper ions and methylene Blue in a single and Binary System on Wheat straw. *Journal Chemical Engineering Data*. 54 3229-3234.
- [10] O. D. Uluzlu., O.D. Sari and M. Tuzen. (2010). Biosorption of antimony from aqueous solution by lichen (*Physcia tribacia*). *Chemical Engineering Journal* 163 382 -388.
- [11] S. Pradhan, S. Singh and L.C. Rai. (2007). Characterization of various functional groups present in the capsule of *Microcystis* and study of their role in biosorption of Fe, Ni and Cr. *Bioresource Technology* 98 595-60.
- [12] X.F. Sun, S.G. Wang, X.W. Liu, W.X. Gong, N. Bao, B.Y. Gao and H.Y. Zhang. (2008). Biosorption of Malachite Green from aqueous solutions onto aerobic granules: Kinetic and equilibrium studies. *Bioresource Technology* 99: 3475-3483.
- [13] N. Ertugay and Y.K. Bayhan. (2008). Biosorption of Cr(VI) from aqueous solutions by biomass of *Agaricus bisporus*. *Journal Hazardous Materials* 154 432- 439.
- [14] B. Volesky (2007). Biosorption and me. *Water Research*. 41 4017- 4029.
- [15] J. Kielland. (1937). Effective diameters of unhydrated and hydrated ions. *Journal of American Chemical Society* 59 1675-1678.
- [16] R. Qu., Y. Zhang., C. Sun., C. Wang., C. Ji., H. Chen and P. Yin. (2010). Adsorption of Hg(II) from an Aqueous Solution by Silica-Gel Supported Diethylenetriamine Prepared via Different Routes: Kinetics, Thermodynamics and Isotherms. *Journal of Chemical Engineering Data*. 55 1496–1504.
- [17] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow and C. Saint. (2009). "Kinetic study and equilibrium

- isotherm analysis of Congo red adsorption by clay materials". *Chemical Engineering Journal* 148 354–364.
- [18] T.K. Sen, S. Afroze and H.M. Ang. (2011). Equilibrium, Kinetics and Mechanism of Removal of Methylene Blue from Aqueous Solution by Adsorption onto Pine Cone Biomass of *Pinus radiata*. *Water Air Soil Pollution*. 218:499–515.
- [19] F. Arias and T.K. Sen. (2009). Removal of zinc metal ion ( $Zn^{2+}$ ) from its aqueous solution by kaolin clay mineral: A kinetic and equilibrium study. *Colloids and Surfaces. A* 348 100–108.
- [20] M.M. Abd EI-Latif, A.M. Ibrahim and M.F. El-Kady. (2010). Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite. *Journal American Science* 6(6) 267–283.