

Full Length Research Paper

Kinetic, equilibrium and thermodynamic studies of the biosorption of Ni(II), Cr(III) and Co(II) from aqueous solutions using banana (*Musa acuminata*) leaf

N. A. Adesola Babarinde^{1*}, J. Oyebamiji Babalola², John Adegoke¹, Uchechi Maraizu¹, Temitope Ogunbanwo¹ and Fopefoluwa Ogunjinrin¹

¹Department of Chemical Sciences, Olabisi Onabanjo University, Ago-Iwoye, Nigeria.

²Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

Accepted 31 January, 2012

The biosorption of Ni(II), Cr(III) and Co(II) by banana (*Musa acuminata*) 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 because 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 analysed with Freundlich and Langmuir isotherm models, and in each case, the Langmuir model appears to have better regression coefficients than the Freundlich model. 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 the metal ions is endothermic and the order of spontaneity of the biosorption process being Ni(II)>Cr(III)>Co(II). Similarly, positive change in entropy was observed for each and the order of disorder is Co(II)>Ni(II)>Cr(III).

Key words: Biosorption, banana, Ni(II), Cr(III), Co(II).

INTRODUCTION

Different industrial processes like mining operations, sludge disposal, metal plating and the manufacture of electrical equipment lead to the release of metal ions, such as Ni(II), Cr(III) and Co(II) into the environment. 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 when compared with the conventional methods of removing them from effluents which are rather expensive with associated demerits. Different agricultural wastes have been investigated for their potentials to remove

these metal ions from solution in order to determine their possible usage in treating industrial effluents (Sari et al., 2007; Anayurt et al., 2009; Babarinde et al., 2008a, b, Babarinde, 2011; Sari and Tuzen, 2008a, b, 2009; Uluozlu et al., 2008; Babarinde et al., 2009; Babarinde and Babalola, 2010a; Chakravarty et al., 2010; Liu et al., 2010; Uluozlu et al., 2010; Zhang and Wang, 2010; Vijayaraghavan and Balasubramanian, 2010; Fiorentin et al., 2010; Qu et al., 2010; Basu et al., 2010). Banana (*Musa acuminata*) is a plant that is grown across the world for its fruit. However, the leaf 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).

*Corresponding author. E-mail: solababarinde@yahoo.com.
Tel: +234-8037232934.

METHODOLOGY

Biomass preparation

Banana (*M. acuminata*) 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 0.5 cm. The leaf sample was kept dry till time of usage.

Preparation of solution

All chemicals (BDH, England) 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 (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 to 4000 cm^{-1} using a Shimadzu FT-IR model 8400S spectrophotometer.

Batch biosorption study

The biosorption study was carried out by contacting 0.5 g of the banana leaf with 25 ml 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 was 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 0.5 g of banana leaf with 25 ml of 100 mg/L metal ion solution in a boiling tube within the pH range of 1 to 7. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1 M HNO_3 and/or 0.1 M NaOH. The boiling tubes containing the mixture were left in a water bath for 6 h. 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 banana leaf was studied at various time intervals (0 to 360 min) and at a concentration of 100 mg/L. This was done by weighing 0.5 g of banana leaf into each boiling tube and 25 ml of 100 mg/L of metal ion solution at optimal pH was introduced into it. The leaf was left in the 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 concentration on biosorption

Batch biosorption study of metal ion was carried out using a concentration range of 10 to 100 mg/L. This was done by introducing 0.5 g of the banana leaf into each of the boiling tubes employed and 25 ml 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 banana 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 to 50°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 25 ml of 100 mg/L 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 analysis

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 banana leaf

The FT-IR spectra of dried unloaded, Ni-loaded, Cr-loaded and Co-loaded banana leaf were taken to obtain information on the nature of possible interactions between the functional groups of banana 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 -OH, -NH, -CH, P=O, -C-O- and -C-N- groups as shown in Figure 1. These bands are due to the functional groups of banana 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 banana 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 and NH_2) which are able to interact with cations (Pradhan et al., 2007; Bueno et al., 2008; Sun et al., 2008; Ertugay and Bayhan, 2008; Uluozlu et al., 2008). This implies that these functional groups would serve in the removal of

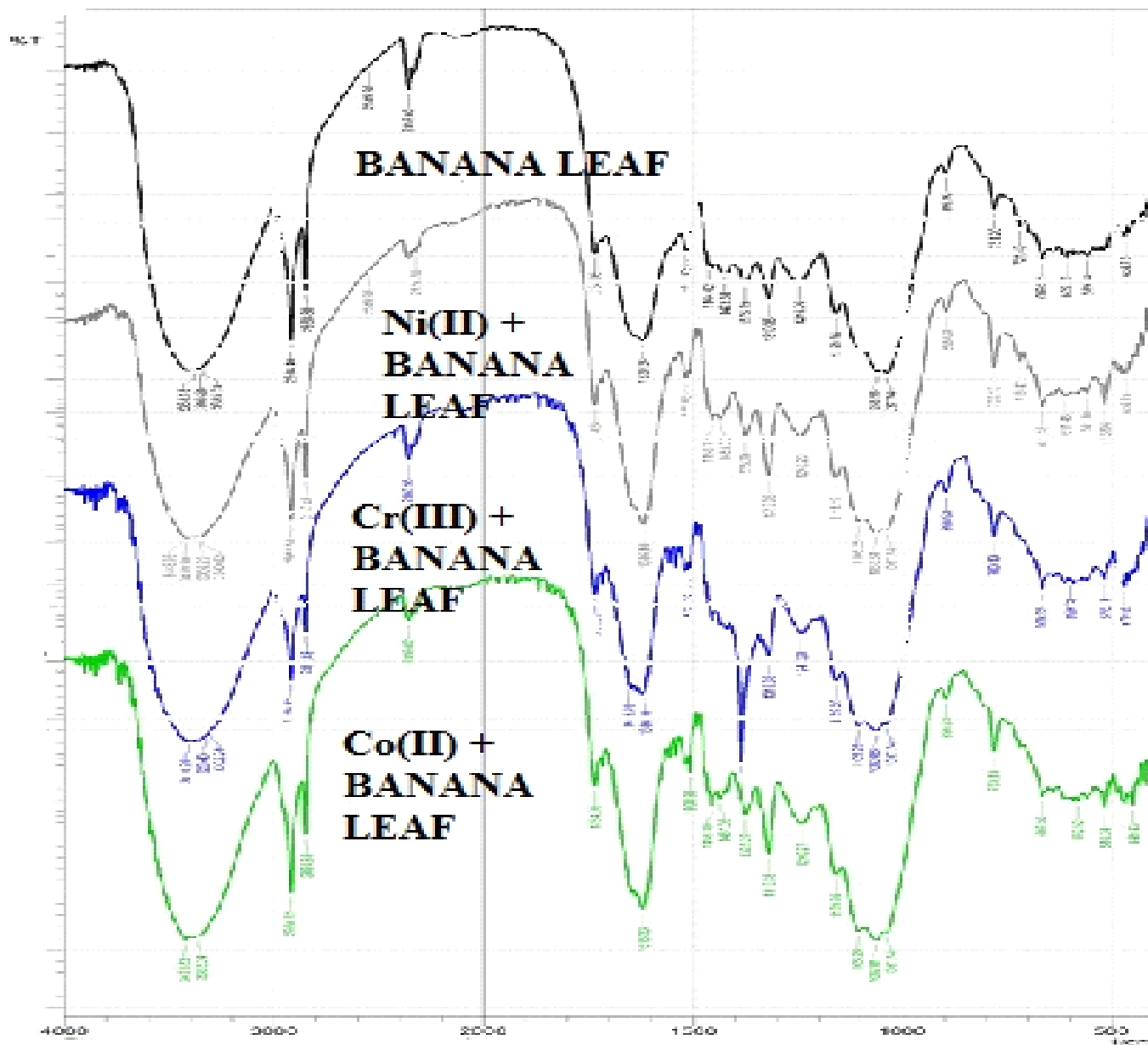


Figure 1. FT-IR spectra of the free and metal-bound banana leaf.

positively charged ions from solution.

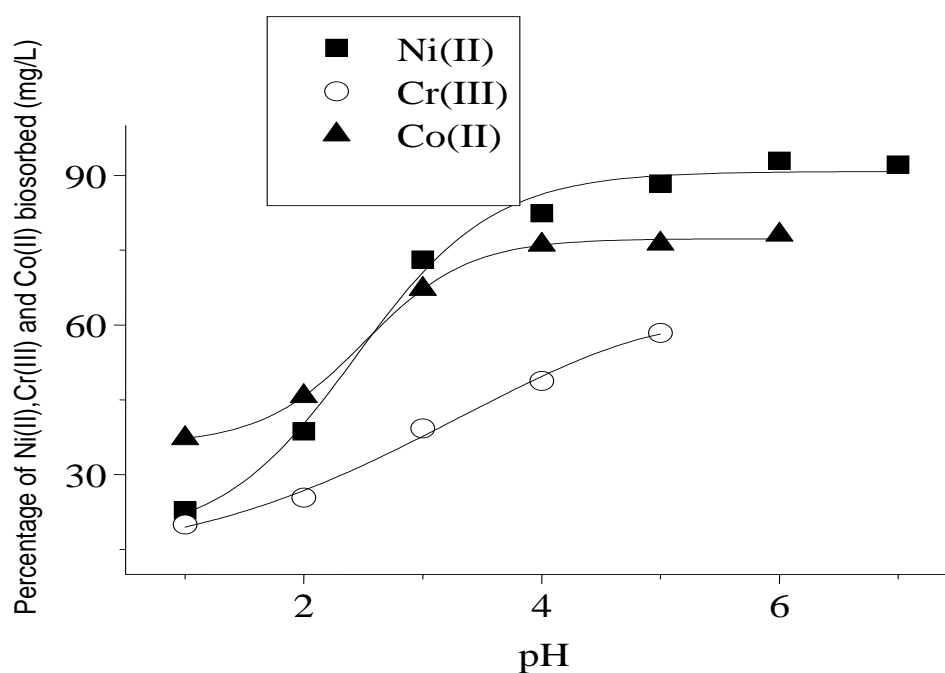
Effect of solution pH on metal ion biosorption

The pH of the 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 banana leaf at various solution pH values. In each case, the biosorption increased steadily as the pH increased from pH 1 to 4. The increase observed in the biosorption with increase in

Table 1. FT-IR spectra characteristics of banana (*M. acuminata*) leaf before and after biosorption of Ni(II), Cr(III) and Co(II) for 2 h.

Metal ion	Absorption band peak (cm^{-1})			Functional group
	Before	After	Difference	
Ni(II)		3419.90	34.72	N-H Stretch (Amine)
Cr(III)	3385.18	3410.26	25.08	N-H Stretch (Amine)
Co(II)		3362.04	23.14	N-H Stretch (Amine)
Ni(II)		1734.06	0	C=O, Stretch (Ester)
Cr(III)	1734.06	1734.06	0	C=O, Stretch (Ester)
Co(II)		1734.06	0	C=O, Stretch (Ester)
Ni(II)		1616.40	3.86	N-H Bend (Amine)
Cr(III)	1620.26	1653.05	32.79	C=C Stretch (Alkene)
Co(II)		1618.33	1.93	N-H Bend (Amine)
Ni(II)		1319.35	0	C-O Stretch (Carboxylic)
Cr(III)	1319.35	1319.35	0	C-O Stretch (Carboxylic)
Co(II)		1319.35	0	C-O Stretch (Carboxylic)
Ni(II)		1062.81	3.85	C-O-C Stretch (Dialkyl, Ester)
Cr(III)	1058.96	1105.25	46.29	C-O-C Stretch (Dialkyl, Ester)
Co(II)		1062.81	3.85	C-O-C Stretch (Dialkyl, Ester)
Ni(II)		1062.81	25.07	C-O Stretch (Alcohol)
Cr(III)	1037.74	1037.74	0	C-O Stretch (Alcohol)
Co(II)		1037.74	0	C-O Stretch (Alcohol)

**Figure 2.** pH-dependent profile of the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf.

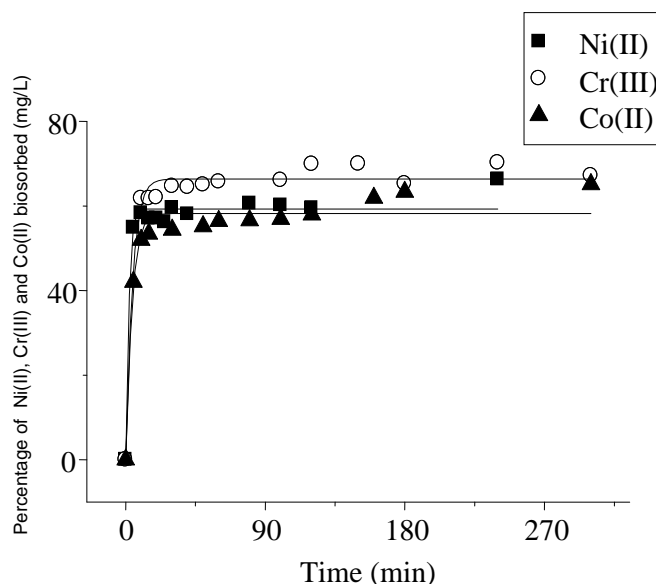


Figure 3. Time course of the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf.

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 in Equation 1 for a divalent metal ion in the 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.

Biosorption kinetics

Figure 3 illustrates the dynamic biosorption process of the three metal ions on banana leaf. It is observed that the biosorptive quantities of the three metal ions on banana 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 h, although, their rates of uptake are different. This might be due to the differences in hydrated ionic sizes of the metal ions (Kielland, 1937).

Several kinetic models are needed to establish the mechanism of a biosorption process. In order to investigate the kinetics of the biosorption of these metal ions on banana leaf, three kinetic models were employed. These are the pseudo-first-order, the pseudo-second-order and the Elovich 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):

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

This 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) 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 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:

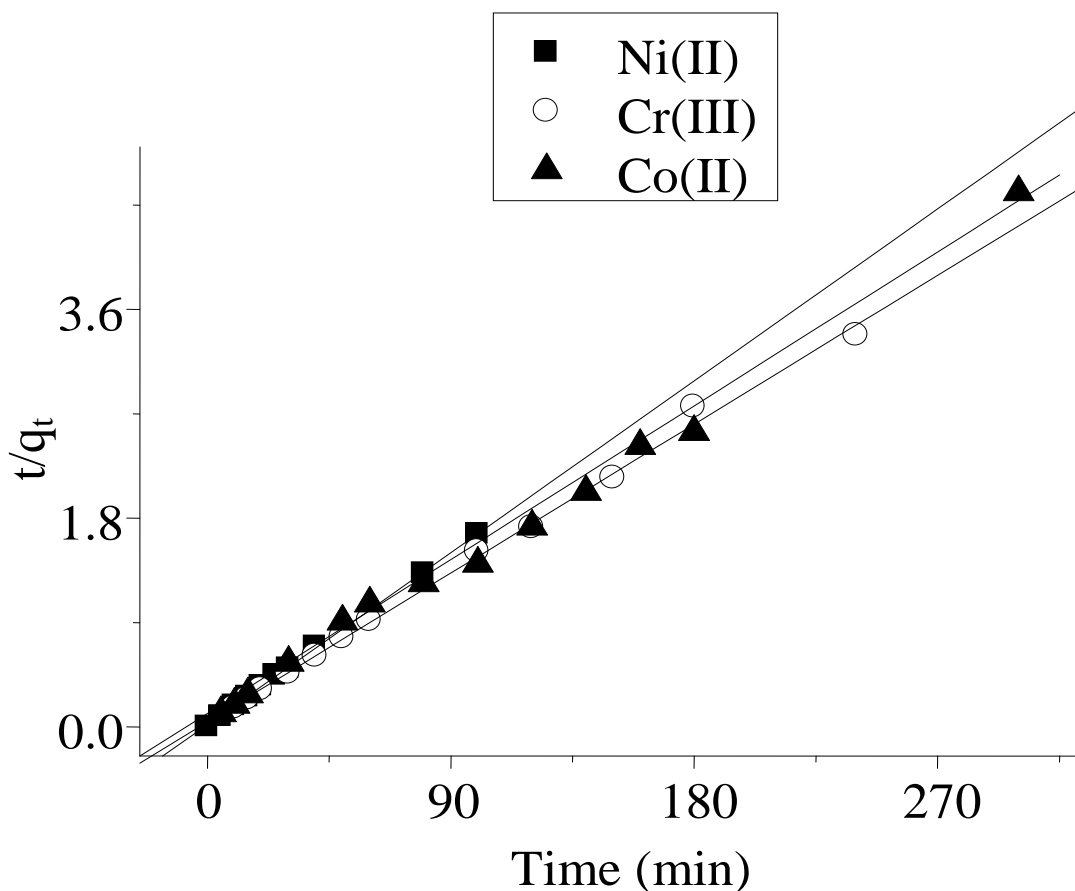


Figure 4. The pseudo-second-order kinetic plot for the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf at 27°C.

Table 2. Parameters of the pseudo-second-order kinetic model for the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf.

Metal ion	k_2 (g/mg/min)	q_e (mg/g)	R^2	SD
Ni(II)	4.2890×10^{-3}	65.3168	0.9996	0.065
Cr(III)	4.658×10^{-3}	70.126	0.99704	0.0604
Co(II)	1.94×10^{-3}	65.1467	0.9941	0.09984

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

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 (g/mg/min). 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 is as shown in Figure 4. The data were equally subjected to the Elovich kinetic model given by:

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

The correlation coefficients were found to be highest for the pseudo-second-order kinetic equation and also each is in excess of 0.99 as presented in Table 2.

On comparison of the values of R^2 for the experimental points, 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 banana leaf. The result shows

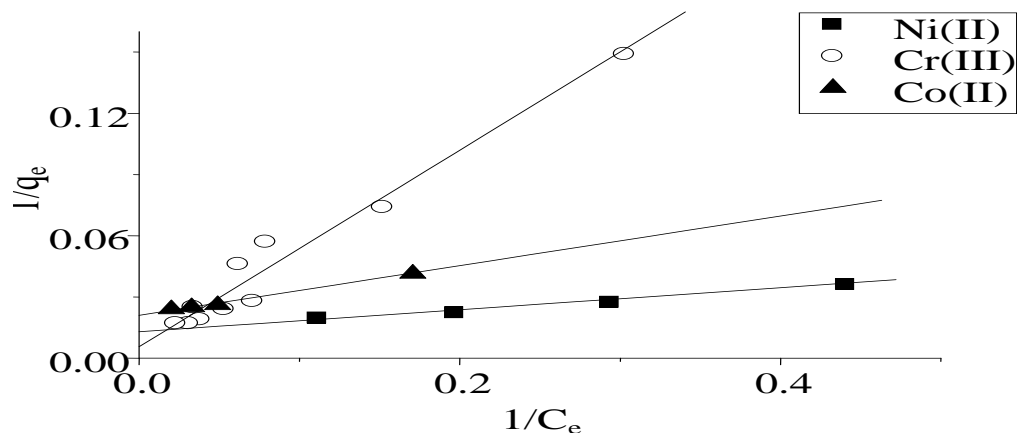


Figure 5. Langmuir isotherm for biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf.

Table 3. Langmuir isothermal parameters for the biosorption of Ni(II), Cr(III) and Co(III) by banana leaf.

Metal ion	Langmuir parameter			
	Γ_m	b_m	R^2	SD
Ni(II)	77.279	19.5924	0.9866	0.0010
Cr(III)	179.21	0.0118	0.9641	0.0083
Co(II)	8.6274	47.2843	0.9947	0.0007

that the rate of biosorption of the metal ions is of the order Cr(III)>Ni(II)>Co(II) which may be due to the differences in hydrated ionic sizes of the ions in the solution (Kielland, 1937). The trivalency of Cr(III) is definitely responsible for it having the fastest rate of biosorption to the banana leaf. 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.

The biosorption capacity for the three metal ions is at least three times the value reported for the biosorption of cadmium ions by banana peel (Kaewsam et al., 2008).

Biosorption isotherm

Figure 5 illustrates the biosorption isotherm of Ni(II), Cr(III) and Co(II) on banana 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:

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \quad (10)$$

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:

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \quad (11)$$

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.

The Γ_m values show that the uptake of the metal ions is of the order Cr(III)>Ni(II)>Co(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 as shown in Figure 6. The plots show that the biosorption efficiency of the biomass increases with increase in the initial

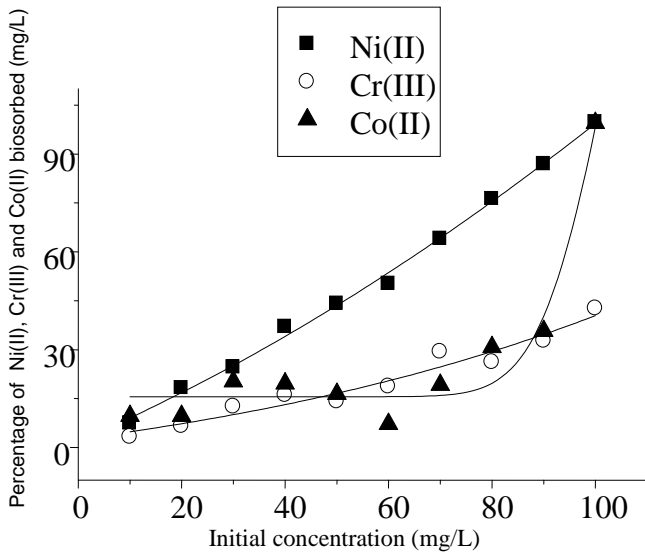


Figure 6. Effect of initial metal ion concentration on the biosorption of Ni(II), Cr(III) and Co(II) using banana (*M. acuminata*) leaf.

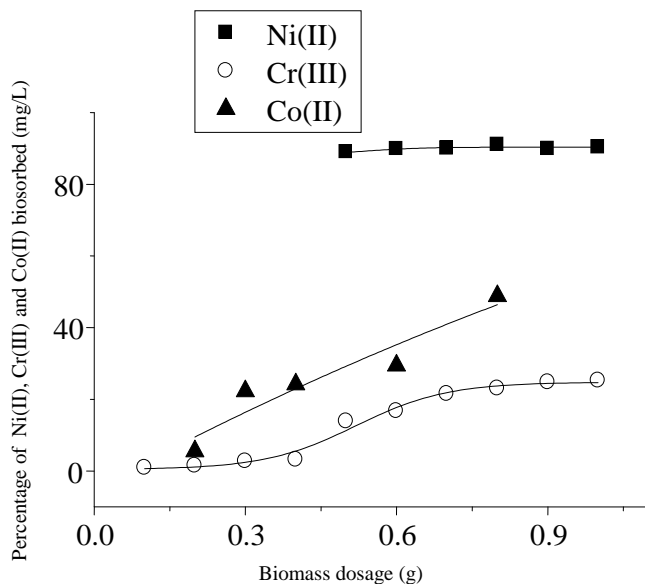


Figure 7. Effect of biosorbent dosage on the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf at 100 mg/L initial metal ion concentration.

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. 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:

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \quad (12)$$

where C_i and C_e are the initial and the equilibrium metal ion concentrations (mg/L), respectively.

The percentage metal ions biosorbed compares favorably well with the values reported for the biosorption of Pb(II), Cu(II), Zn(II) and Ni(II) by banana peel (Ashrat et al., 2011).

Effect of biomass dosage on biosorption

The effect of biomass dosage on biosorption efficiency is as shown 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).

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

$$\Delta G^\circ = RT \ln K_c \quad (13)$$

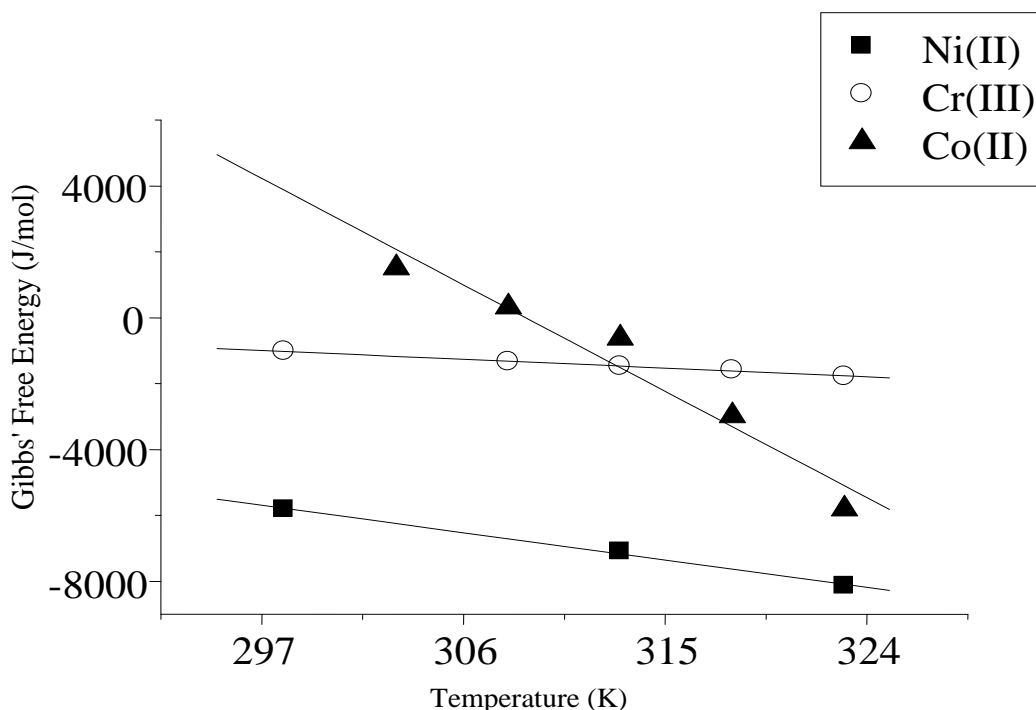
where T (K) is the absolute temperature. The equilibrium constant (K_c) was calculated from the following relationship.

$$K_c = \frac{C_{ad}}{C_e} \quad (14)$$

where C_e and C_{ad} are the equilibrium concentrations of metal ions (mg/L) in solution and on biosorbent, respectively. Consequently, the thermodynamic behaviour of the biosorption of Ni(II), Cr(III) and Co(II) onto banana 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 (Qu et al., 2010; Uluoğlu et al., 2010) (Table 4). The change in free energy is related to other thermodynamic properties

Table 4. Thermodynamic parameters for the biosorption of Ni(II), Cr(III) and Co(II) by banana leaf.

Metal ion	ΔH° (kJ/mol)	ΔS° (J/mol/K)	R^2	SD
Ni(II)	21.68	92.17	0.9968	93.44
Cr(III)	7.78	29.55	0.9960	20.64
Co(II)	110.08	358.90	0.9493	757.27

**Figure 8.** Thermodynamic plots for the biosorption of Ni(II), Cr(III) and Co(II) by banana (*M. acuminata*) leaf.

as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

where T is the absolute temperature (K); R is the gas constant (8.314 J/mol/K). ΔH° (J/mol) and ΔS° (J/mol/K) were calculated from the slope and intercept of the linear plot of $\ln K_c$ versus $1/T$. The thermodynamic parameters obtained for this study are as shown in Table 4. The plots shown in Figure 8 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 Ni(II)>Cr(III)>Co(II). The positive values of ΔH° for the biosorption of the three metal ions suggest

endothermic nature of the biosorption processes. 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 Cr(III)< Ni(II)<Co(II).

Conclusions

In this work we studied the biosorption of Ni(II), Cr(III) and Co(II) by banana 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 Langmuir isotherm model. The thermodynamic study shows that the biosorption of each of Ni(II), Cr(III) and Co(II) was spontaneous, endothermic and chaotic in the order Cr(III)< Ni(II)<Co(II).

REFERENCES

- Anayurt RA, Sari A, Tuzen M (2009). Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass. Chem. Eng. J., 151(1-3): 255-261.
- Ashrat MA, Wajid A, Mahmood K, Maah MJ, Yusoff I (2011). Low cost biosorbent banana peel (*Musa sapientum*) for the removal of heavy metals. Sci. Res. Essays, 6(19): 4055-4064.
- Babalola JO, Babarinde NAA, Popoola OA, Oninla VO (2009). Kinetic, isothermal and thermodynamic studies of the biosorption of Ni(II) and Cr(III) from aqueous solutions by *Talinum triangulare* (Water leaf). Pac. J. Sci. Technol., 10(1): 439-450.
- Babarinde NAA, Babalola JO (2010a). Kinetic, Equilibrium and Thermodynamic studies of the biosorption of Cd(II) and Pb(II) from solutions using Siam leaf (*Chromolaena odorata*). Int. Rev. Chem. Eng., 2(1): 18-24.
- Babarinde NAA, Babalola JO, Adegboye KA (2008a). Kinetic, isotherm and thermodynamic studies of the biosorption of cadmium(II) snail shell. J. Appl. Sci. Res., 4(11): 1420-1427.
- Babarinde NAA, Babalola JO, Adeyemi OO, Oyesiku OO (2010b). Kinetic, Isothermal and Equilibrium studies of the biosorption of Pb(II) from solutions a Moss (*Stereophyllum radiculosum*). Pac. J. Sci. Technol., 11(2): 471-479.
- Babarinde NAA, Babalola JO, Onafalajo OA (2008b). Kinetic, equilibrium and thermodynamic studies of the biosorption of lead(II) from solution by *Calymperes erosum*. Pac. J. Sci. Technol., 9(2): 630-637.
- Babarinde NAA (2011). Kinetic, equilibrium and thermodynamic studies of the biosorption of Pb(II), Cd(II) and Cr(III) by Neem leaf. J. Innov. Res. Eng. Sci., 2(5): 291- 306.
- Babarinde NAA, Babalola JO, Ogunfowokan AO, Onabanjo AC (2009). Kinetic, equilibrium and thermodynamic studies of the biosorption of cadmium(II) from solution by *Stereophyllum radiculosum*. Toxicol. Environ. Chem., 91(5): 911-922.
- Basu T, Gupta K, Ghosh U C (2010). Equilibrium and Thermodynamics on arsenic (III) sorption Reaction in the Presence of background Ions occurring in Groundwater with nanoparticle Agglomerates of Hydrous Iron (III) + Chromium (III) Mixed Oxide. J. Chem. Eng. Data, 55: 2039-2047.
- Bueno BYO, Torem ML, Molina F, de Mesquita LMS (2008). Biosorption of lead(II), chromium (III) and copper (II) by *R. opacus*: Equilibrium and kinetic studies. Miner. Eng., 21: 65-75.
- Chakravarty P, Sarma NS, Sarma HP (2010). Biosorption of cadmium (II) from aqueous solution using heartwood powder of *Areca catechu*. Chem. Eng. J., 162: 949- 955.
- de la Rosa G, Reynel-Avila H E, Bonilla-Petriciolet A, Cano-Rodríguez I, Velasco-Santos C, Martínez-Elangovan R, Pilip L, Chandraraj K (2008). Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies. J. Hazard. Mater., 152: 100-102.
- Ertugay N, Bayhan YK (2008). Biosorption of Cr(VI) from aqueous solutions by biomass of *Agaricus bisporus*. J. Hazard. Mater., 154: 432-439.
- Fiorentin LD, Trigueros DEG, Modenes AN, Espirnoza-Quinones FR, Pereira N C, Barros STD, Santos OAA (2010). Biosorption of reactive blue 5G dye onto drying orange bagasse in batch system: Kinetic and equilibrium modelling. Chem. Eng. J., 163: 68-77.
- Kaewsam P, Salkaew W, Wongcharee,S (2008). Dried Biosorbent Derived from Banana Peel: A Potential Biosorbent for Removal of Cadmium ions from Aqueous Solution. The 18th Thailand Chemical Engineering and Applied Chemistry Conference. www.app.eng.ubu.ac.th/~resproject/upload/.../11.paper_1_puttaporn.2 552.
- Kielland J (1937). Effective diameters of unhydrated and hydrated ions. J. Am. Chem. Soc., 59: 1675-1678.
- Liu Y, Sun X, Li B (2010). Adsorption of Hg²⁺ and Cd²⁺ by ethylenediamine modified peanut shells. Carbohydr. Poly., 81: 335-339.
- Pradhan S, Singh S, Rai LC (2007). Characterization of various functional groups present in the capsule of *Microcystis* and study of their role in biosorption of Fe, Ni and Cr. Bioresour. Technol., 98: 595-601.
- Qu R, Zhang Y, Sun C, Wang C, Ji C, Chen H, Yin P (2010). Adsorption of Hg(II) from an Aqueous Solution by Silica-Gel Supported Diethylenetriamine Prepared via Different Routes: Kinetics, Thermodynamics and Isotherms. J. Chem. Eng. Data, 55: 1496-1504.
- Sari A, Tuzen M (2008a). Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater., 157(2-3): 15 448-454.
- Sari A, Tuzen M (2008b). Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater., 160(2-3): 349-355.
- Sari A, Tuzen M (2009). Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. J. Hazard. Mater., 164(2-3): 1004-1011.
- Sari A, Tuzen M, Uluözülü ÖD, Soylyak M (2007). Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass. Biochem. Eng. J., 37(2): 151-158.
- Sun X F, Wang SG, Liu XW, Gong WX, Bao N, Gao BY, Zhang HY (2008). Biosorption of Malachite Green from aqueous solutions onto aerobic granules: Kinetic and equilibrium studies. Bioresour. Technol., 99: 3475-3483.
- Uluözülü ÖD, Sari A, Tuzen M, Soylyak M (2008). Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. Bioresour. Technol., 99(8): 2972-2980.
- Uluozlu OD, Sari A, Tuzen M (2010). Biosorption of antimony from aqueous solution by lichen (*Phyiscia tribacia*). Chem. Eng. J., 163: 382-388.
- Vijayaraghavan K, Balasubramanian R (2010). Single and binary biosorption of cerium and europium onto crab shell particles. Chem. Eng. J., 163: 337-343.
- Wu Y, Zhang L, Gao C, Ma X, Han R (2010). Adsorption of copper ions and methylene Blue in a single and Binary System on Wheat straw. J. Chem. Eng. Data, 54: 3229-3234.
- Zhang J, Wang A (2010). Adsorption of Pb(II)from Aqueous Solution by Chitosan-g-poly(acrylic acid)/Attapulgitte/Sodium Humate Composite Hydrogels. J. Chem. Eng. Data, 55: 2379-2384.