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Full Length Research Paper

Kinetic, isotherm and thermodynamic studies of the biosorption of zinc (II) from solution by maize wrapper

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The removal of Zn^{2+} from dilute aqueous solution using maize (*Zea mays*) wrapper as the biosorbent is reported in this paper. Batch experiments were carried out to assess biosorption kinetic and equilibrium behaviour of Zn^{2+} by varying parameters such as pH, contact time and initial metal ion concentration at 27ºC. The analysis of residual metal ions was determined using atomic absorption spectrophotometer. The pH study shows that the initial pH would play a vital role in the biosorption of the Zn^{2+} from solution. The optimum pH obtained was in the range pH 5 - 7, therefore pH 6 was used for other studies. The kinetic study shows that uptake of Zn^{2+} increased with time and that maximum biosorption was obtained within 60 min of the process. The result obtained showed that the pseudo-first order model correlated with the experimental data better than the pseudo-second order model examined in this study. Freundlich and Langmuir isotherm models were used to analyse the experimental data of the biosorption process. The Freundlich and Langmuir equations obtained are $\log \Gamma = 0.643 \log C_e + 1.1177$ and $1/\Gamma = 0.0411/C_e + 0.009$, respectively. The correlation factors are 0.9971 and 0.9889, respectively. The free energy change for the biosorption of Zn^{2+} at 27ºC, initial concentration of 100 mg L^{-1} and pH 6 is –7.663 kJ mol^{-1} within 60 min. These results indicate that maize wrapper has potential for the removal of Zn^{2+} from industrial wastewater.

Key words: Biosorption, Zn(II), isotherm, maize wrapper, kinetic studies.

INTRODUCTION

Contamination of the environment by heavy metals has been on the increase due to industrial revolution of the last few decades. Heavy metal ions detected in waste streams from mining operations, tanneries, electronics, electroplating and petrochemical industries are the major environmental problem in both developed and developing countries (Akhtar et al., 2004). Consequently, there has been adverse effect on our environment, because of the toxicity of the heavy metals involved (Marques et al., 2000).

Biosorption has been considered to be an alternative technique for the uptake of toxic metal ions from waste-water. It is a relatively new technology that has found application in the removal of low-level concentration of toxic metal. It is more economical than conventional methods such as ion exchange and chemical precipitation. The use of biomass of plant or animal origin for the biosorption process has been given much attention in the recent years (Akhtar et al., 2004; Solisio et al., 2006; Babarinde et al., 2006,2007a,b; Barros et al., 2007; Has-san et al., 2007; Iqbal and Saeed, 2007; King et al., 2007). The biosorbents are cheap materials often with high affinity and capacity for binding the metal ions (Con-rad and Hansen, 2007). The mechanism of the biosorp-tion process has been explained in terms of the reaction between anionic groups present in the biomasses and the cationic metal ions (Pradhan et al., 2007).

In this study, the removal of Zn (II) ions from aqueous solution using maize wrapper was investigated. The objective was to study the influence of different sorption conditions in the uptake of Zn (II) by maize wrapper.

MATERIALS AND METHODS

Materials

The maize (*Zea mays*) wrapper used as the biosorbent were obtained as dry wrappers from a farm in Ijebu-Imusin, Ogun State, Nigeria. The dry wrappers were rinsed with distilled water, sun-dried and cut into pieces. They were kept in a dry place till the time of usage. Analytical grade of $ZnSO_4$ was used for the study. Stock

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solution of 1000mg L^{-1} Zn(II) was prepared from $ZnSO_4$. The solutions used for the study were obtained by dilution of the stock solution to the required concentrations. The initial pH of each of the solutions was adjusted to the optimum pH value by drop-wise addition of 0.1 M HNO_3 and/or 0.1 M NaOH, except for the experiment on the effect of pH where the study was carried out at different pH values. Fresh dilution of the stock solution was done for each biosorption study.

Biosorption studies

Each of the batch biosorption studies was carried out by contacting the biomass with the metal ions under different conditions for a period of time in a glass tube. Studies were conducted at 27ºC to determine the effects of initial solution pH, contact time and initial ion concentration on the biosorption of Zn (II) ions. Each experiment was conducted in a thermostated water bath (Haake Wia model) and the residual metal ions analysed using Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP). The amount of metal ions biosorbed from solution was determined by difference and the mean value was calculated for each set of experiments.

Effect of pH

The effect of pH on the biosorption of metal ions was carried out within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). It has been reported that the suitable pH ranges for the sorption of different metal ions were slightly different. As a result, the suitable pH ranges for Cu(II), Cd(II), Zn(II) and Pb(II) ions should be 1-6, 1-8, 1-7 and 1-7.5, respectively. The procedure used is similar to those earlier reported (Vasuderan et al., 2003; Xu et. al., 2006; Babarinde et al., 2006). Experiments were conducted at 27ºC to study the effect of initial solution pH on the biosorption of Zn(II) by contacting 0.5 g of the maize wrapper with 50 mL of 100 mg L^{-1} zinc(II) solution in a glass tube. The pH of each of the solutions was adjusted to the desired value with 0.1 M sodium hydroxide and /or 0.1 M nitric acid. The studies were conducted at pH values of 2 - 7. The glass tubes containing the mixture were left in a water bath for 24 h. The biomass was removed from the solution by decantation and the residual Zn(II) concentration in the solution was analyzed. All studies were conducted in triplicates and the mean value was determined for each. Subsequent biosorption experiments were performed at the optimum pH 6.

Effect of contact time

The biosorption of the Zn(II) by maize wrapper was studied at various time intervals (0-120 min). A constant concentration of 100 mg L^{-1} was used. 0.5 g of maize wrapper was weighed into glass tubes and 50 mL of solution at the optimum pH was added into each tube. The maize wrapper in each tube was removed from the solution by decantation after a given time interval and the residual ions in the solution was determined. The amount of metal ions biosorbed was calculated for each sample. The mean of the three results for a particular time was then calculated and plotted against time.

Effect of concentration

Batch biosorption study was carried out using a concentration range of 10 - 100 mg L^{-1}. 0.5 g of the maize wrapper was weighed into each of the glass tubes employed and 50 mL of the metal ion solution at the optimum pH was added. Three glass tubes were used for a particular concentration. The biosorption mixture was then left in a water bath to maintain the temperature at 27ºC for a period of optimum contact time required to reach equilibrium. The maize wrapper was removed from the mixture by decantation and the residual ions in the solution were determined. The biosorption capacity (q_e) of the sludge is expressed as milligrams of biosorbed ions per gram of dry mass of the biomass (mg g^{-1}) and the removal efficiency of metallic ion (%E) were calculated by equations (1) and (2), respectively.

$$q_e = \left(\frac{C_i - C_e}{m} \right) V \qquad \text{.............. (1)}$$

$$\%E = 100 \frac{C_i - C_e}{C_i} \qquad \text{................(2)}$$

where C_i is the initial metal ion concentration (mg L^{-1}); C_e, the equilibrium metal ion concentration (mg L^{-1}); m, the mass of the biosorbent (g); V, the volume of the solution (L).

The results obtained were analysed using both Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in linearised form is

$$\log \Gamma = \frac{1}{n} \log C_e + \log K \qquad \text{............(3)}$$

where n and K are Freundlich constants. The linearised form of the Langmuir isotherm is

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \qquad \text{.................... (4)}$$

where b_m is a coefficient related to the affinity between the sorbent and sorbate, and Γ_m is the maximum sorbate uptake under the given condition.

RESULTS AND DISCUSSION

The effect of pH on biosorption

The pH study showed that maximum sorption occurred at pH 5 - 7 as shown in Figure 1. The percentage Zn(II) biosorbed was slightly lower at lower pH values. This further confirms the earlier report about the optimum pH range for Zn(II). Under acidic conditions, both the biosorbent and the metal ion are positively charged thereby causing electrostatic repulsion (Goel et al., 2005). Decrease in pH (increase in the concentration of H^+) causes increase in competition with the positively charged metal ions. On the other hand, increase in pH (decrease in H^+ concentration), results in increase in metal ion uptake.

Generally, as a result of net negative charge on the different functional groups in the cell wall of the biosorbent above the isoelectric point, the ionic state of the different ligands such as carbonyl, phosphate and amino groups favours reaction with Zn^{2+}. On the other hand, on decreasing pH, the net charge on the cell wall is positive thereby inhibiting the approach of positively charged ions (Gõksungur et al., 2005). As the pH increased, the ligand

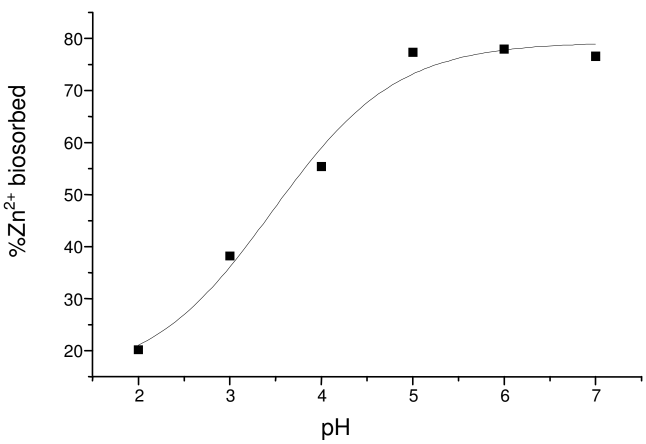

Figure 1. Effect of pH on biosorption of Zn^{2+} by maize wrapper at 100 mg L^{-1} and 27°C.

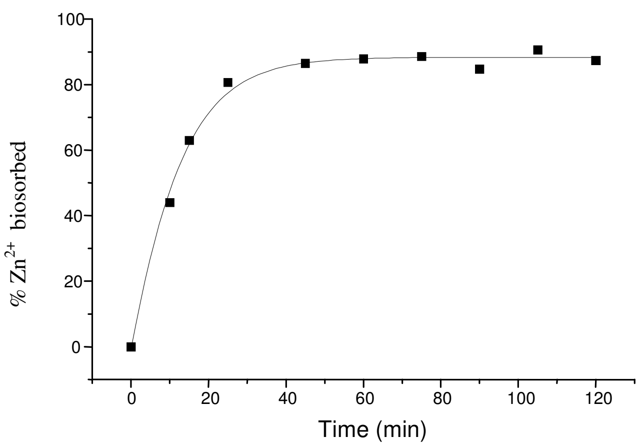

Figure 2. Time course of Zn^{2+} biosorption by maize wrapper at 100 mg L^{-1}, 27°C and pH 6.

in maize wrapper would be exposed, increasing the attraction of metal ions with positive charge and allowing the biosorption on the wrapper surface. The result suggests that initial pH would play a vital role in the removal of Zn^{2+} from aqueous solutions using maize wrapper.

Kinetics of the biosorption process

As shown in Figure 2, the biosorption of Zn(II) onto the biomass was rapid for the first 30 min and equilibrium was reached within 60 min. The period of 60 min was therefore considered as the optimum time. The reaction involved the biosorption of metal ion (represented as M^{2+}) from the liquid phase to the solid phase and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below:

$$S_{wrapper} + M^{2+} \leftrightarrow S_{wrapper} - M^{2+}$$

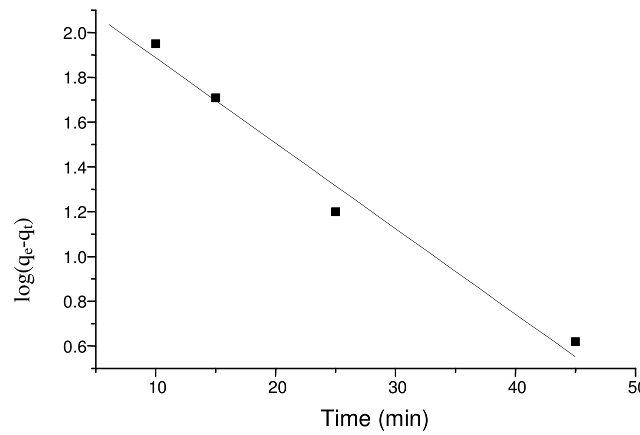

Figure 3. Pseudo-first order plot for the biosorption of Zn(II) by maize wrapper at 27°C and pH 6.

Therefore, the pseudo-first order kinetic model was used to establish the rate of reaction.

The pseudo-first order and pseudo-second order rate equations (Goel et al., 2005; Kavitha and Namasivayam, 2007) were applied to the kinetic study as shown below in equations (1) and (2), respectively.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad ......(6)$$

where k_1 is the Lagergren rate constant of the biosorption (min^{-1}); k_2 is the pseudo-second order rate constant (g mg^{-1} 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 $\log(q_e\text{-}q_t)$ vs t for the biosorption of Zn(II) ions on the maize wrapper at initial concentration of 100 mg L^{-1} obey the pseudo-first order reversible kinetics. The overall rate constant of the biosorption (k_1) was calculated from the slope of the plot. As shown in Figure 3, it was found that the pseudo-first order equation better described the biosorption process because negative value of rate constant was obtained for the pseudo-second order equation. Therefore, the biosorption kinetics could well be approximated more favourably by pseudo-first order kinetic model for Zn(II). Lagergren constants obtained for this study are presented in Table 2. The q_e and k_1 obtained in this study were more than 8 and 35 times the values earlier reported for the sorption of Pb(II) by carbon aerogel, respectively (Goel et al., 2005).

The effect of initial Zn^{2+} concentration on biosorption

The effect of initial Zn^{2+} concentration on the biosorption efficiency of maize wrapper under optimum conditions of

Table 1. Freundlich and Langmuir isothermal adsorption parameters for the biosorption of Zn^{2+} ions at 27ºC and pH 6 using maize wrapper.

Freundlich parameters				Langmuir parameters			
$\frac{1}{n}$	K	R	S.D.	b_m	Γ_m	R	S.D.
1.555	13.1129	0.9971	0.025	24.331	111.111	0.9889	0.001

Table 2. Pseudo-first order kinetic model parameters for the biosorption of Zn^{2+} by maize wrapper at 27ºC and pH 6.

$q_e(mgg^{-1})$	$k_1(Lmin^{-1})$	R^2	S.D.
184.2808	0.0868	0.9793	0.104

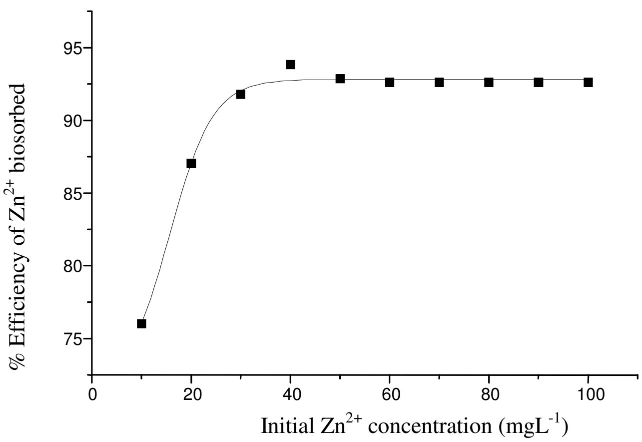

Figure 4. Efficiency plot for the biosorption of Zn^{2+} by maize wrapper at 27ºC and pH 6

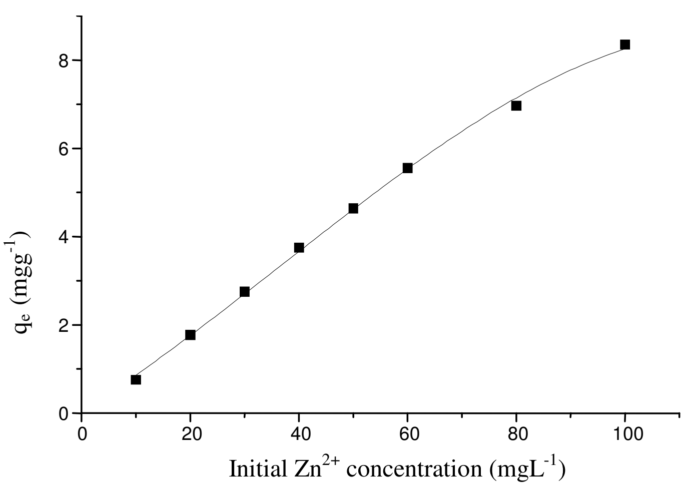

Figure 5. Effect of initial concentration on the biosorption capacity of Zn(II) by maize wrapper.

pH and contact time is shown in Figure 4. The biosorption efficiency increased with increase in Zn(II) initial concentration but reached a plateau at 50 mg L-1. The plateau value obtained showed that as the metal/biomass ratio increases there is a decrease in biosorption efficiency. This can be attributed to the saturation of the available binding sites on the biomass. As the number of metal ions competing for the fixed binding sites on the biomass increases, the resultant effect is reduction in the complexation of the metal with the biomass. This implies that the higher the concentration the more the amount of Zn(II) that was left in solution. The mechanism of the biosorption process involved ion exchange between H^+ and metal ions (represented as M^{2+}) at the surface of the biosorbent. For a biosorbent having carboxyl functional groups, the reaction mechanism has been shown (Goel et al., 2005) to be

$$2C_xOH^+ + M^{2+} \rightleftharpoons (C_xO)_2M^{2+} + 2H^+$$

An increase in the concentration of metal ions would cause more H^+ to be released thereby causing decrease in pH. This would invariably lead to decrease in biosorption efficiency at high metal ion concentrations. Similarly, the uptake capacity of Zn(II) by maize wrapper was calculated and plotted against initial Zn(II) concentration as shown in Figure 5. The result showed increase in the biosorption capacity as the initial Zn(II) concentration increased but equilibrium was approached at the concentration of 100 mgL^{-1}.

The experimental data were also applied to both the Freundlich and Langmuir isotherm models as shown in Figs. 6 and 7, respectively. The data fitted well into both the Freundlich and Langmuir isotherms. The Freundlich and Langmuir equations obtained are $\log \Gamma = 0.643 \log C_e + 1.1177$ and $1/\Gamma = 0.0411/C_e + 0.009$, respectively. The correlation factors are 0.9971 and 0.9889, respectively. The isothermal biosorption parameters for these isotherms are shown in Table 1. The Freundlich and Langmuir parameters obtained (Table 1) compare well with those of other biosorbents that have been reported (Akar and Tunali, 2006; Kavitha and Namasivayam, 2007). The values of the parameters show that maize wrapper is a good biosorbent for the removal of zinc(II) from wastewaters.

Thermodynamics of the biosorption process

The biosorption of Zn(II) is reversible (Han et al., 2006) and as such can be represented by apparent

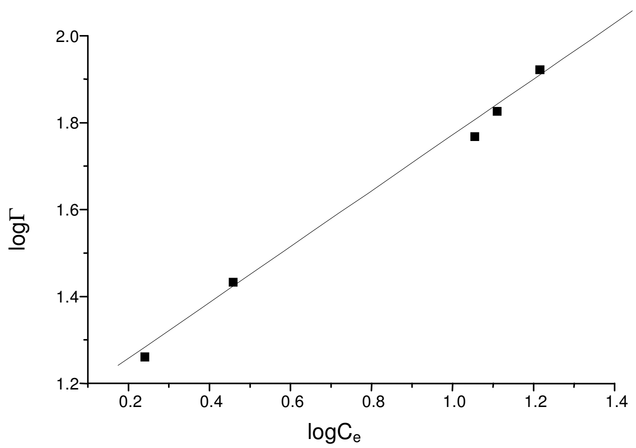

Figure 6. The linearized Freundlich biosorption isotherm of Zn^{2+} by maize wrapper at 27°C and pH 6.

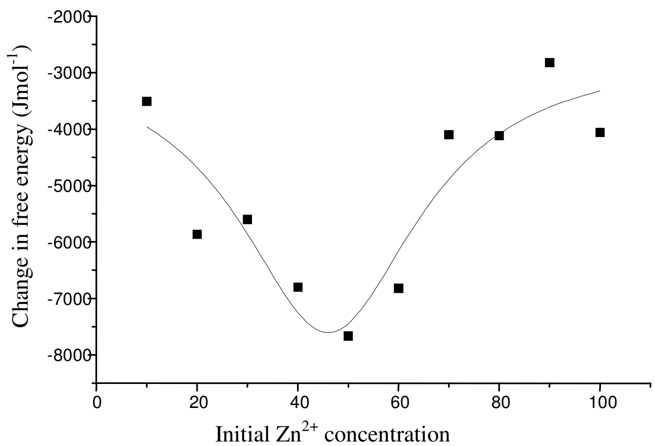

Figure 8. Change in free energy in the biosorption of Zn^{2+} by maize wrapper at 27°C and pH 6.

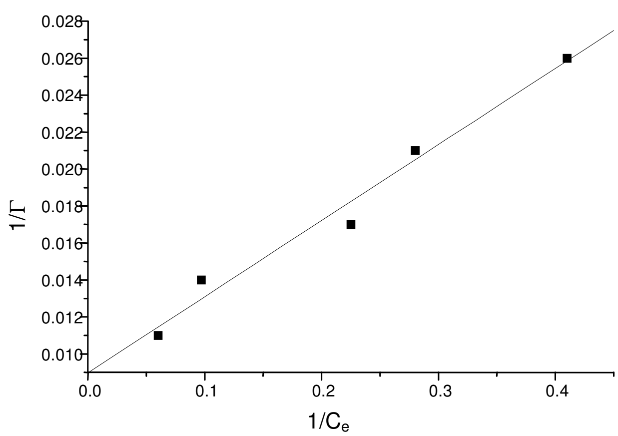

Figure 7. The linearized Langmuir biosorption isotherm of Zn^{2+} by maize wrapper at 27°C and pH 6.

equilibrium constant, K_c.

$$K_c = \frac{C_{ad}}{C_e} \quad \text{.................................} \quad (5)$$

The Gibbs free energy of biosorption is thus obtained as

$$\Delta G^{\circ} = -RT \ln K_c \quad \text{..........................} \quad (6)$$

where ΔG° is standard Gibbs free energy change for the biosorption (kJ mol^{-1}), R the universal gas constant (8.314 J mol^{-1} K^{-1}) and T the temperature (K). The free energy change for the biosorption of Zn (II) at 27ºC, initial concentration of 100 mg L^{-1} and pH 6 is –7.663 $kJmol^{-1}$. The large negative value of ΔG° obtained for the biosorption of Zn (II) shows the spontaneity of each biosorption process. The value is comparable to those earlier reportted (Kavitha and Namasivayam, 2007). Batch biosorption study shows that the free energy change is dependent on the initial concentrations as shown in Figure 8. The result shows decrease in free energy change with increase in initial concentration until a minimum was reached at the concentration of 50 mg L^{-1}. Thermodynamically, the process was most spontaneous at this concentration at the temperature of 27°C. The efficiency study also confirmed this concentration as the optimum concentration as shown in section 3.3.

Conclusions

The batch biosorption studies have shown that the biosorption is pH dependent and the optimum pH for the removal of Zn(II) using maize wrapper is in range 5 - 7. Maximum biosorption was obtained within the first 60 min of the process. Kinetic study also showed that the biosorp tion is well represented by pseudo-first order equation. The amount of zinc ions biosorbed increased with increase in initial metal ion concentration. Thermodynamically, the biosorption was most spontaneous at 50 mg L^{-1}. Maize wrapper, an agricultural waste could therefore, be used as potential biosorbent for the removal of Zn (II) from aqueous solutions.

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REFERENCES

Akar T, Tunali S (2006). Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution. Bioresour. Technol 97: 1780-1787.

Akhtar N, Iqbal J, Iqbal M (2004). Enhancement of lead biosorption by microalgal biomass immobilized onto Loofa (*Luffa cylindrical*) sponge.

Eng. Life Sci. 4(2): 171-178.
Babarinde NAA, Babalola JO, Sanni RA (2006). Biosorption of lead ions from aqueous solution by maize leaf. Int. J. Phys. Sci. 1(1): 23-26.
Babarinde NAA, Babalola JO, Sanni SO (2007a). Isotherm and thermodynamic studies of the biosorption of Cd(II) from solution by maize leaf. Int. J. Phys. Sci. 2(8): 207-211.
Babarinde NAA, Oyesiku OO, Dairo OF (2007b). Isotherm and thermodynamic studies of the biosorption of copper (II) ions by *Erythrodontium barteri*. Int. J. Phys. Sci. 2(11): 300-304.
Barros AJM, Prasad S, Leite VD, Souza AG (2007). Biosorption of heavy metals in upflow sludge columns. Bioresour. Technol. 98: 1418-1425.
Conrad K, Hansen HCB (2007). Sorption of zinc and lead on coir. Bioresour. Technol. 98: 89-97.
Freundlich HMF (1906). Ueber die adsorption in Lloesungen. Z. Physic. Chem. A57: 385-470.
Goel J, Kadirvelu K, Rajagopal C, Garg K (2005). Investigation of adsorption of lead, mercury and nickel from aqueous solutions onto carbon aerogel. J. Chem. Technol. Biotechnol. 80: 469-476.
Gõksungur Y, Üren S, Güvenc U (2005). Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast. Bioresour. Technol. 96(1): 103-109.
Han R, Li H, Li Y, Zhang J, Xiao H, Shi J (2006). Biosorption of copper and lead ions by waste beer yeast. J. Hazard. Mater. B137: 1569-1576.
Hassan SH, Talat M, Rai S (2007). Sorption of cadmium and zinc from aqueous solutions by water hyacinth (*Eichchornia crassipes*). Bioresour. Technol. 98: 918-928.
Iqbal M, Saeed A (2007). Production of an immobilized hybrid biosorbent for the sorption of Ni(II) from aqueous solution. Proc. Biochem. 42: 148-157.
Kavitha D, Namasivayam C (2007). Experimental and kinetic studies on ethylene blue adsorption by coir pith carbon. Bioresour. Technol. 98: 14-21.
King P, Rakesh N, Beenalahari S, Kumar YP, Prasad VSRK (2007). Removal of lead from aqueous solution using *Syzygium cumini* L.: Equilibrium and kinetic studies. J. Harzard. Mater. 142: 340-347.
Langmuir I (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc. 40: 1361-1403.
Marques PASS, Rosa MF, Pinheiro HM (2000). pH effects on the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution by waste brewery waste. Bioproc. Eng. 23: 135-141.
Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF (2006). Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}, using dried marine green macroalga *Caulerpa lentilligera*. Bioresour. Technol. 97: 2321-2329.
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.
Solisio C, Lodi A, Torre P, Converti A, Borghi MD (2006). Copper removal by dry and rehydrated biomass of *Spirulina platensis*. Bioresour. Technol. 97: 1756-1760.
Vasuderan P, Padmavathy V, Dhingra SC (2003). Kinetics of biosorption of cadmium on Baker's yeast. Bioresour. Technol. 89(3): 281-287.
Xu H, Liu Y, Tay J (2006). Effect of pH on nickel biosoprtion by aerobic granular sludge. Bioresour. Technol. 97(3): 359-363.