Isotherm and Thermodynamic Studies of the Biosorption of Zinc (II) from Solution by Maize Leaf.

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ABSTRACT

The removal of Zn(II) ions from dilute aqueous solution using maize (*Zea mays*) leaf as the adsorbent is reported in this paper. The effects of pH, contact time, and initial metal ion concentrations were studied at 27 C. The analysis of residual metal ions was determined using atomic absorption spectrophotometer. The result of the pH study shows that the initial pH would play a vital role in the removal of the metal ions from solution. The optimum pH obtained was in the range pH 4-7. Kinetic studies show that the uptake of zinc ions increases with time and that maximum adsorption was obtained within the first 40 minutes of the biosorption process. The adsorption isotherms obtained at 27 C and optimum pH fitted well into both the Freundlich and Langmuir isotherms. The Freundlich and Langmuir equations are $\log \Gamma = 1.7833 \log C_e + 0.1316$ and $1/\Gamma = 0.0423/C_e - 0.3565$, respectively. The correlation factors are 0.9964 and 0.9974, respectively. The free energy change for the biosorption of Zn(II) at 27 C, initial concentration of 100 mgL^{-1} and pH 4 -7 is –5.4525 kJ mol^{-1}. These results indicate that maize leaf has potential for the removal of zinc ions from industrial wastewater.

(Keywords: biosorption, Zn(II), zinc, Freundlich isotherm, Langmuir isotherm, maize leaf)

INTRODUCTION

Contamination of the environment by heavy metals has been on the increase due to the industrial development of the last few decades; consequently, there has been an adverse effect on our environment because of the toxicity of the heavy metals involved (Marques et al., 2000). Both air and water have been found contaminated by heavy metals as a result of smelting processes in various industries. Water is particularly vulnerable to contamination from discharge of waste by various industries. Water pollution due to heavy metals is an issue of great environmental concern (Vasuderan et al., 2003).

Heavy metal ions are present in the wastewaters of some chemical industries such as pulp and paper mills, petrochemical manufactures, and refineries (Pamukoglu and Kargi, 2007). Heavy metal ions such as cobalt, copper, nickel, chromium, and zinc are detected in waste streams from mining operations, tanneries, electronics, electroplating, and petrochemical industries, as well as in textile mill production (Patterson and Passino, 1987). Heavy metals have a harmful effect on human physiology and other biological systems when they exceed the tolerance levels. Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders. These metals are toxic both in chemically combined forms as well as their elemental forms.

The conventional methods used to remove heavy metals include chemical precipitation, ion exchange, electrodialysis, membrane separations, reverse osmosis, and solvent extraction (Matlock et al., 2002; Feng et al., 2000; Mohammadi et al., 2005). The search for new, effective and economical technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost (Abia et al., 2003; Ajmal et al., 2003; Aksu, 2002; Annadurai et al., 2002; Babarinde and Oyedipe, 2001; Babarinde et al. 2002; Babarinde, 2002; Babarinde et al. 2006; Bansode et al., 2003; Cimino et al., 2000; Demirbas, 2003; Feng and Aldrich, 2004; Fourest and Roux, 1992; Akar and Tunali, 2005; Han et al., 2006; Southichak et al., 2006; Pavasant et al., 2006; Liu et al., 2006; Green-Ruiz, 2006; Tsui et al., 2006; Wang and Chen, 2006; Lu et al., 2006; Chang et al., 2006; Guibaud et al., 2006).

The increasing contamination of aquatic resources with heavy metals has initiated the search for cheaper and newer strategies for their removal (Pradham et al., 2007). Biosorption has been found to be an alternative to conventional methods such as precipitation, ion-exchange, solvent extraction, liquid membrane, and electrochemical processes of treating solutions having metal ions. The biosorbents are cheap materials often with high affinity and capacity for binding the metal ions (Conrad and Hansen, 2007).

Of interest in this study is the removal of Zn(II) ions from aqueous solution using maize leaf. The objective was to study the influence of uptake of Zn(II) by maize leaf under different sorption conditions.

MATERIALS

The maize leaves (*Zea mays*) used as the biosorbent for this study were obtained as dry leaves from a farm in Ijebu-Imusin, Ogun State, Nigeria. The dry leaves were rinsed with distilled water, sun-dried, and cut into pieces. They were kept in a dry place until the time of usage.

The chemicals used for the study were analytical grades of $ZnSO_4$, NaOH, and HNO_3. Stock solutions of 1000mgL^{-1} Zn(II) were 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 0.1M HNO_3 and/or 0.1M NaOH, except for the experiment of 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. The uptake capacity of Zn(II) in batch system was studied in a systematic way in this work. Studies were conducted at 27 C to study the effect of initial solution pH, contact time and initial ion concentration on the biosorption of Zn(II) ions.

Each experiment was conducted in a thermo-regulated water bath (Haake Wia model) and the residual metal ions analysed using Atomic Absorption Spectrophotometer (Buck Scientific model 210 VGP). The amount of metal ions biosorbed from solution was determined by difference. The mean value was also calculated.

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 are 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 procedures used are similar to those earlier reported (Vasudevan et. al., 2003 and Xu et. al., 2006; Babarinde et al., 2006).

Experiments were conducted at 27 C to study the effect of initial solution pH on the adsorption of the metal ions by contacting 0.5 g of the maize leaf with 50 ml of 100 mgL^{-1} zinc(II) solution in a glass tube. The pH of each of the solutions was adjusted to the desired value with 0.1M sodium hydroxide or 0.1M nitric acid.

The studies were conducted at pH values of 2, 3, 4, 5, 6 and 7. The glass tubes containing the mixture were left in a water bath for 24 hours. The biomass was removed from the solution by filtration 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 using the optimum pH.

EFFECT OF CONTACT TIME

The biosorption of the Zn(II) by maize leaf was studied at various time intervals (0-120 min). A constant concentration of 100 mg/l was used. 0.5g of maize leaf was weighed into thirty-six glass tubes and 50 ml of solution at the optimum pH was added into each tube. The maize leaf in a set of three tubes was then filtered at different time intervals. The filtrates were then analysed. 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

The batch biosorption study was carried out using a concentration range of 10 – 100 mgL^{-1}. 0.5g of the maize leaf was weighed into each of the 30 glass tubes employed and 50ml of the metal ion solution at the optimum pH was measured into each glass tube containing the maize leaf. Three glass tubes were used for a particular concentration. The biosorption mixture was then left in a water bath to maintain the temperature (27 C) for optimum contact time required to reach equilibrium time. The maize leaf was removed from the mixture by filtration and the residual ions in the solution were determined. The removal efficiency of the metal ion was calculated as

$$\% \text{ Removal} = 100 (C_i - C_e) / C_i \quad \textbf{(1)}$$

where C_i is initial metal ion concentration (mgL^{-1}) and C_e the equilibrium metal ion concentration (mgL^{-1}).

The results obtained were equally analyzed using both Freundlich (Freundlich, 1907) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in linearized form is:

$$\log \Gamma = (1/n)\log C_e + \log K \quad \textbf{(2)}$$

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

$$\frac{1}{\Gamma} = \frac{1}{b_m}\frac{1}{C_e} + \frac{1}{\Gamma_m} \quad \textbf{(3)}$$

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

Several factors affect the sorption of heavy metals onto the surface of biomass. Factors such as pH, contact time, initial metal ion concentration, temperature, and common ions have been reported (Akar and Tunali, 2006; Han et al., 2006; Southichak et al., 2006; Pavasant et al., 2006; Liu et al., 2006). The results of the three different studies are shown in Figures 1-5.

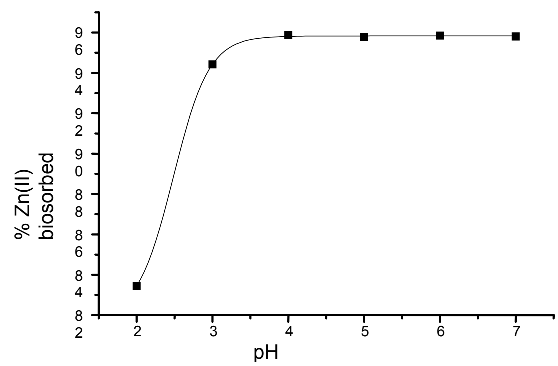

Figure 1: Effect of pH on Sorption Behavior of Zn(II) Sorption by Maize Leaf.

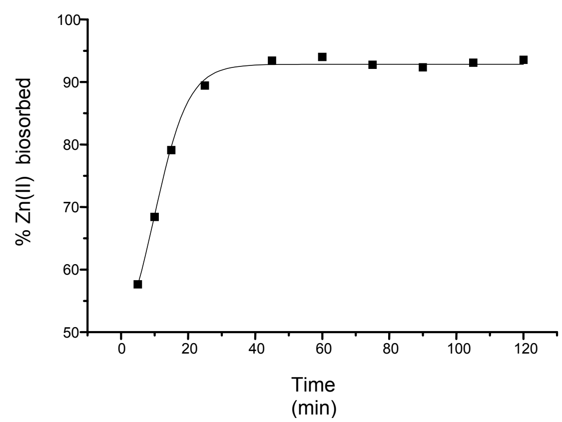

Figure 2: Time Courses of Zn (II) Removal by Maize Leaf.

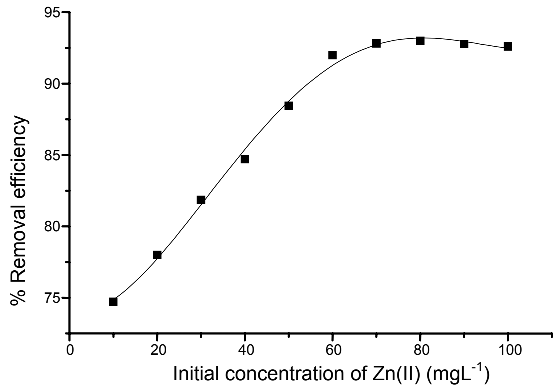

Figure 3: The Efficiency of Maize Leaf in the Biosorption of Zn(II).

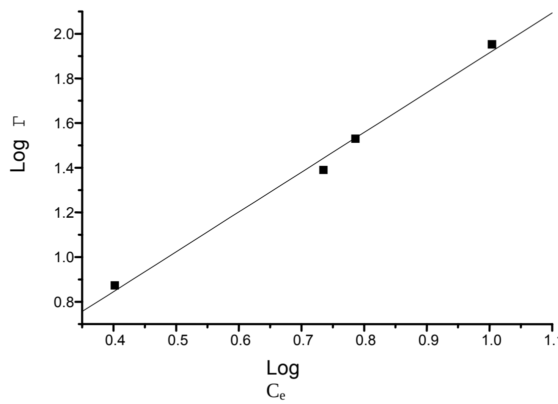

Figure 4: The Linearized Freundlich Biosorption Isotherm of Zn (II) Using Maize Leaf.

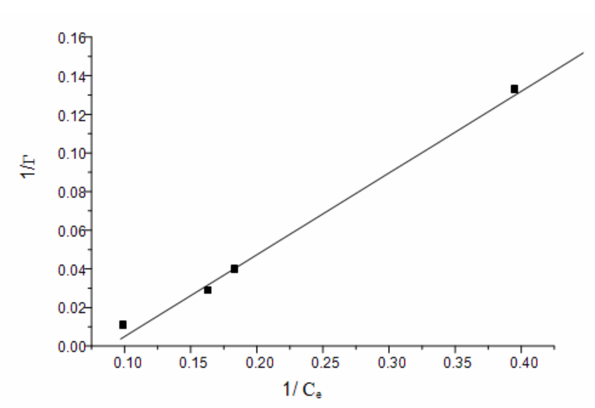

Figure 5: The Linearized Langmuir Biosorption Isotherm of Zn (II) Using Maize Leaf.

EFFECT OF pH ON BIOSORPTION CAPACITY

The result of the pH study shows that maximum sorption occurred at pH 4-7 (Figure 1). The percentage Zn(II) biosorbed is slightly lower at lower pH values. This further confirms the earlier report about the optimum pH range for Zn(II). As a result of net negative charge on the cell wall of the biosorbent above, the isoelectric point of the ionic state of the ligands such as carbonyl, phosphate, and amino groups favors 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 charge ions (Gõksungur et al., 2005). As the pH increased, the ligands in maize leaf would be exposed, increasing the attraction of metal ions with positive charge and allowing the biosorption on the leaf surface. The result suggests that optimum biosorption is obtained at pH 4.0 to 7.0 and that initial pH would play a vital role in the removal of Zn^{2+} from aqueous solutions using maize leaf.

EFFECT OF CONTACT TIME

The effect of contact time on the biosorption of Zn(II) ions is shown in Figure 2. From the plot, it is seen that the adsorptive capacity of Zn(II) increased with increase in contact time. The biosorption of Zn(II) onto the biomass was rapid for the first 30 min and equilibrium was nearly reached within the first 40 min. The period of 60 min was therefore considered as the optimum time.

THE EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial metal ion concentration on the biosorption of capacity of maize leaf was studied under optimum conditions of pH and contact time as shown in Figure 3. The biosorption of zinc increased with increase in the initial metal ion concentration but reaches a peak at 70 mgL^{-1}.

The peak value obtained shows 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. The implication is that the higher the concentration the more the amount of metal ions that will be left in solution.

The same experimental data were applied to both the Freundlich and Langmuir isotherm models as shown in Figures 4 and 5, respectively. The data fitted well into both the Freundlich and Langmuir isotherms. The Freundlich and Langmuir equations are $\log \Gamma = 1.7833 \log C_e + 0.1316$ and $1/\Gamma = 0.0423/C_e - 0.3565$, respectively.

The correlation factors are 0.9964 and 0.9974, respectively. The isothermal biosorption parameters for these isotherms are shown in Table 1.

The Freundlich and Langmuir parameters obtained compare well with those of other adsorbents that have been reported (Akar and Tunali, 2006). The values of the parameters show that maize leaf is a good biosorbent for the removal of Zn from wastewaters.

The effect of metal ion concentration on biosorption capacity showed that maize leaf biomass biosorbed these metal ions from solution. The amount of metal ions adsorbed increased with increase in initial metal ion concentration.

Table 1: Freundlich and Langmuir Isothermal Adsorption Parameters for the Biosorption of Zn^{2+} ions at 27 C and pH 4 using Maize Leaf.

Freundlich Parameters			
1/ n	**K**	**R**	**S.D.**
1.7833	**1.3539**	**0.9964**	**0.0464**
Langmuir Parameters			
b_m	**Γ_m**	**R**	**S.D.**
23.64	**2.805**	**0.9974**	**0.0048**

THERMODYNAMICS OF THE BIOSORPTION PROCESS

The biosorption of these metal ions is reversible (Han et al., 2006) and as such can be represented by apparent equilibrium constant, K_c.

$$K_c = C_{ad}/ C_e \quad \textbf{(4)}$$

The Gibbs free energy of biosorption is thus obtained as:

$$\Delta G^{\circ} = -RT\ln K_c \quad \textbf{(5)}$$

Where ΔG° is standard Gibbs free energy change for the biosorption ($kJmol^{-1}$), 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 27 C, initial concentration of 100 mgL^{-1} and pH 4 -7 is –5.4525 kJ mol^{-1}. The large negative value of ΔG° obtained for the biosorption of Zn(II) shows the spontaneity of each biosorption process.

CONCLUSION

The batch biosorption studies have shown that the biosorption is pH dependent and the optimum pH for the removal is in the range of 4-7. The amount of zinc ions biosorbed increased with increase in initial metal ion concentration. Maximum adsorption was obtained within the first 40 minutes. Maize leaf biomass, an agricultural waste, could therefore be used as potential biosorbent for the removal of Zn(II) from aqueous solutions.

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