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Full Length Research Paper

Isotherm and thermodynamic studies of the biosorption of Cd(II) from solution by maize leaf

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The removal of Cd(II) from dilute solutions using maize (Zea mays) leaf as the biosorbent was studied. The effects of pH, contact time and initial metal ion concentration on the biosorption were monitored. The residual Cd(II) in solution was determined using atomic absorption spectrophotometer. The biosorption was found to be pH-dependent and the optimum pH for the biosorption was pH 3. The biosorption was also time-dependent as maximum biosorption was obtained after 2 h. The Freundlich equation obtained for the biosorption was $\log \Gamma = 0.8775 \log C_e + 1.095$ while the Langmuir equation was $^1/_\Gamma = 0.0982/C_e - 0.0058$. The correlation factors were 0.9943 and 0.9869, respectively. The remo-val efficiency decreases with increase in initial Cd(II) concentration due to reduction in available binding site on the biosorbent for Cd (II). The free energy change for the biosorption at 300 K with an initial Cd(II) concentration of 100 mgL^{-1} and pH 3 was –7.17 $kJmol^{-1}$. These results indicate that maize leaf has potential for the uptake of Cd(II) from industrial effluents.

Key words: Biosorption, Cd (II), adsorption isotherms, maize leaf, Zea mays.

INTRODUCTION

The biosorption of heavy metal ions from industrial wastewater using biomass is currently receiving much attention because of the relatively cheap cost of treat-ment. Biosorption, is based on metal sequestering properties of certain natural materials of biological origin (Bayramoglu et al., 2006). Different agricultural materials have been used in the biosorption of heavy metal ions from solution (Bayramoglu et al., 2006; Guibaud et al., 2006; Lu et al., 2006; Solisio et al., 2006). The potential of some plants materials to remove metal ions, which commonly occur in industrial effluents, has been studied. The effects of ionic strength, contact time, pH and initial metal ion concentration were investigated. (Babarinde and Oyedipe, 2001; Babarinde et al., 2002; Babarinde, 2002; Akar and Tunali, 2006; Han et al., 2006; Tsui et al., 2006; Sawalha et al., 2006; Wang and Chen, 2006) Other materials, which are of animal origin, have equally been used (Vijayaraghavan et al., 2006). The choice of cad-mium for this study was made as a result of the industrial and potential pollution impact of the metal. Cadmium has joined lead and mercury to form the "big three" metals with the greatest potential hazard (Akar and Tunali, 2006). Maize leaf was chosen as the biosorbent because it was previously used for the biosorption of Pb^{2+} (Babarinde et al., 2006)

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MATERIALS AND METHODS

Dry maize (*Zea mays*) leaves were obtained from a farm in Ijebu-Imushin, Ogun State, Nigeria. The leaves were rinsed with distilled water, sun dried and cut into pieces of approximately 0.5 cm. The leaf sample was kept dry till the time of usage. Analytical grade $Cd(NO_3)_2.4H_2O$ was used for the study. A stock solution of 1000 mgL^{-1} Cd(II) was prepared from $Cd(NO_3)_2.4H_2O$. The solutions used for the study were obtained by diluting the stock solution to the required concentrations. The initial pH of each of the solutions was adjusted by drop wise introduction of 0.1 M HNO_3 and/ or 0.1 M NaOH solution to the desired pH. Freshly diluted stock solutions were used for each experiment.

BIOSORPTION STUDY

The biosorption study was carried out by contacting 0.5 g of the maize leaf with 50 ml the solution under different conditions for a

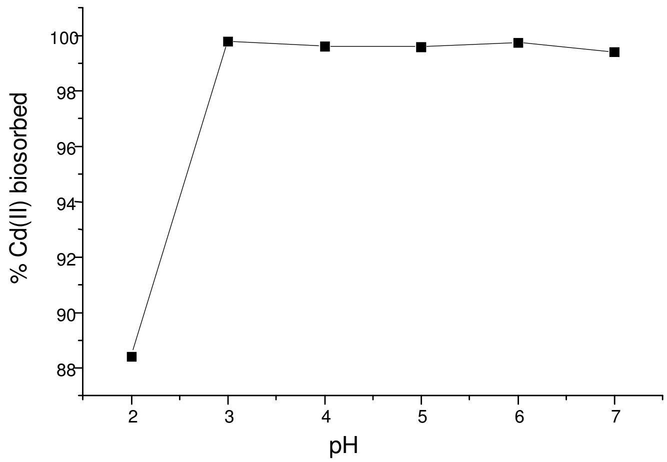

Figure 1. Effect of pH on biosorption of Cd(II) by maize leaf.

period of time in a glass tube. All the studies were conducted at 27°C using a thermostated water bath (Haake Wia Model) to determine the effects of pH, contact time and initial Cd(II) concentration on the biosorption. The residual Cd(II) was analyzed using Atomic Absorption Spectrophotometer (Buck Scientific Model 210 VGP). The amount of Cd(II) biosorbed from solution was determined by difference and the mean value calculated.

Effect of pH

The effect of pH on the biosorption of Cd(II) was carried out within the range that would not be influenced by the metal precipitated (Pavasant et al., 2006). The procedure used is similar to those earlier reported (Vasuderan et al., 2003; Xu et al., 2006; Babarinde et al., 2006). 0.5 g of maize leaf was contacted with 50 ml of 100mgL^{-1} Cd(II) solution in a glass tube. 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 studies were conducted at pH 2, 3, 4, 5, 6 and 7. The glass tubes containing the mixture were left in a water bath for 24 h. The biomass was removed from the solution by filtration and the residual Cd(II) concentration in the solution was analyzed. All experiments were conducted in triplicates and the mean value was determined for each pH.

Effect of contact time

The biosorption of Cd(II) by maize leaf was studied at various time intervals (0 –120 min) at the concentration of 100 mgL^{-1}. This was done by weighing 0.5 g of maize leaf into each glass tube and 50 ml of Cd(II) solution at pH 3 introduced into it.

Effect of initial Cd(II) concentration

The effect of initial Cd(II) on its biosorption was carried out using a concentration range of 10 – 100 mgL^{-1}. 0.5 g of the maize leaf was introduced into each of the glass tubes employed and 50 ml of Cd(II) solution at pH 3 was added to the tubes. Three glass tubes were used for each concentration. The tubes were left in thermostated water bath maintained at 27°C. The maize leaf was removed from the solution and the concentration of residual Cd(II) in each solution was determined. The result obtained was analyzed using Freundlich (Freundlich, 1907) and Langmuir (Langmuir, 1918) isotherms. The linearized form of the Freundlich isotherm is:

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

Where n and K are Freundlich constants. The liberalized form of the Langmuir isotherm is

$$\frac{1}{\Gamma} = \frac{1}{b_m}\frac{1}{C_e} + \frac{1}{\Gamma_m} \quad \text{.................... (2)}$$

Where b_m is a coefficient related to the affinity between the adsorbent and adsorbate while Γ_m is the maximum adsorbate uptake under the given condition. The removal efficiency of the maize leaf was calculated as

$$\% \text{ Removal} = 100\,(C_i - C_e) / C_i \quad \text{........... (3)}$$

Where C_i is the initial Cd(II) concentration (mgL^{-1}), C_e the equilibrium Cd(II) concentration (mgL^{-1})

RESULTS AND DISCUSSION

Effect of solution pH on biosorption

It has been reported that the suitable pH ranges for the sorption of different metal ions were slightly different. Consequently, the suitable pH ranges for Cu(II), Cd(II), Zn(II) and Pb(II) should be 1 – 6, 1 – 8, 1 – 7 and 1 – 7.5 respectively. The result of the pH study given in Figure 1 shows that maximum biosorption was obtained at pH 3. The percentage Cd(II) biosorbed is slightly lower at higher pH values. This result supports the earlier report that the biosorption is pH-dependent (Pavasant et al., 2006). Surface adsorption is a physicochemical phenomenon. The cell walls of many plants consist of polysaccharides, proteins and lipids, hence offer a host of functional groups capable of binding to heavy metals. These functional groups, such as amino, carboxylic, sulphydryl, phosphate and thiol groups, differ in their affinity as well as specificity for metal binding (Liu et al., 2006).

The charges of the adsorbate and that of the adsorbent often depend on the pH of the solution (Han et al., 2006). To understand the biosorption mechanism, the biosorption of Cd^{2+} as a function of pH was measured. It is observed from Figure 1 that there was an increase in the biosorption capacity of the biomass with increase in pH from 2.0 to 3.0 but slightly lower biosorption was obtained at higher pH. As a result of net negative charge on the cell wall of the biosorbent at pH above the isoelectric point, the ionic state of the ligands such as carbonyl, phosphate and amino groups favours reaction with Cd^{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 (Goksungur et al., 2005). As the pH increased, the ligands in maize leaf would be exposed thereby 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 3.0 and that initial pH would play a vital role in the removal of Cd^{2+} from aqueous solutions using maize leaf.

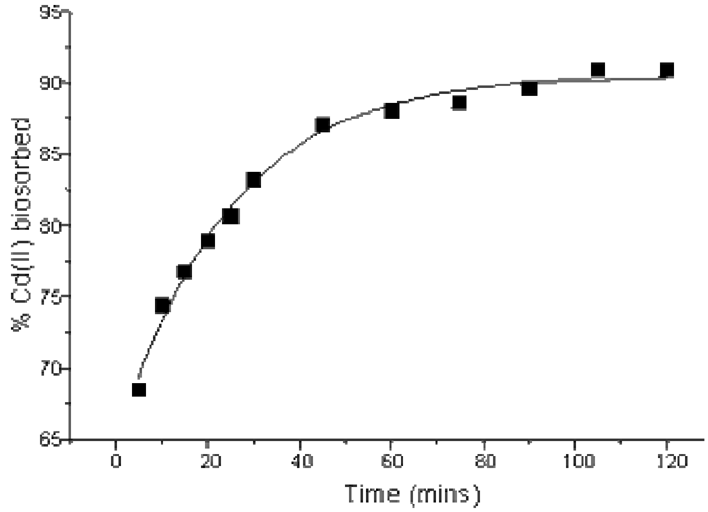

Figure 2. Time course of the biosorption of Cd(II) by maize leaf.

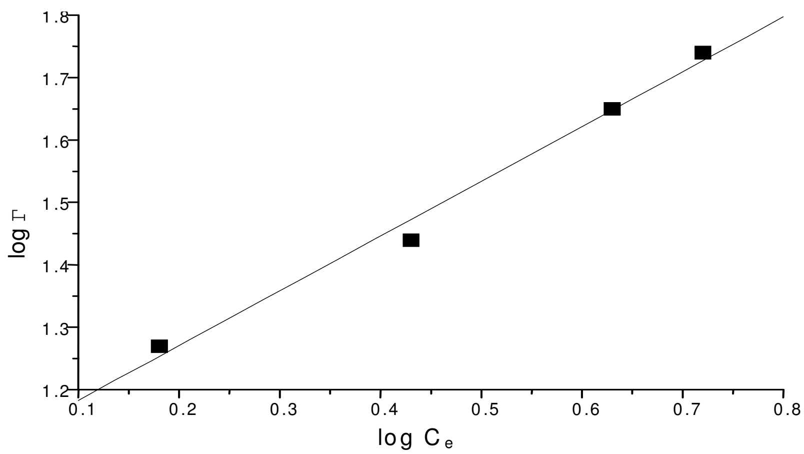

Figure 3. Freundlich Isotherm for the biosorption of Cd(II) by maize leaf

Effect of contact time on the biosorption of Cd (II)

The result of the effect of contact time on the biosorption of Cd(II) from aqueous solution is shown in Figure 2. It is observed that the adsorptive capacity of maize leaf for Cd(II) increased with increase in contact time. The biosorption of Cd(II) by the biomass was rapid for the first 40 min as a result of available binding sites on the biomass. The biosorption approached equilibrium within 120 min as the binding sites were used up. The period of 120 min was therefore taken as the time required for the biosorption of Cd(II) by maize leaf. Biosorption of metal ions has been reported to be biphasic (Liu et al., 2006). The initial fast phase occurs due to surface adsorption on the biomass. The subsequent slow phase occurs due to diffusion of the metal ions into the inner part of the biomass. It is observed in Figure 2 that the biosorption rate was high at the beginning but equilibrium was approached within 120 min, similar to what was earlier reported (Liu et al., 2006).

Effect of initial Cd(II) concentration on biosorption

The effect of initial Cd(II) concentration on the biosorption capacity shows that up to 94.65% of it was biosorbed at the initial concentration of 100 mgL^{-1} within the first 120 min. The efficiency increased with increase in the initial Cd(II) concentration. However, the gradual increase in the efficiency of the biomass shows nearness to saturation of the available binding sites on it. The same experimental data was applied to both the Freundlich and Langmuir isotherm models as shown in Figures 3 and 4, respectively. The data fitted well into both isotherms. The isothermal biosorption parameters for these isotherms are shown in Table 1. These Freundlich and Langmuir

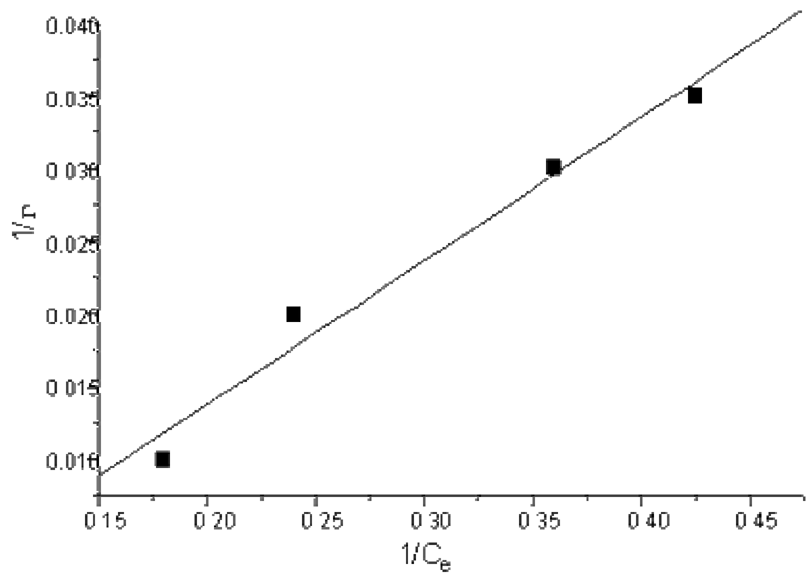

Figure 4. Langmuir isotherm for the biosorption of Cd(II) by maize leaf.

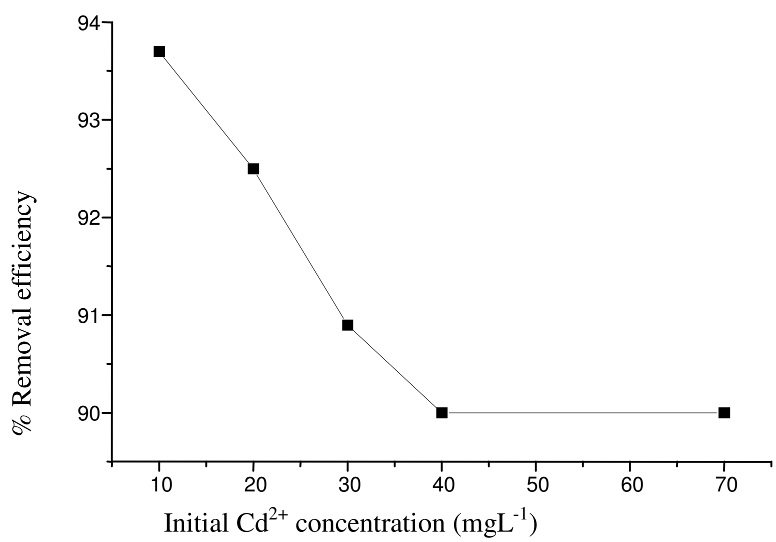

Figure 5. Removal efficiency plot for the biosorption of Cd(II) by maize leaf.

Table 1. Freundlich and Langmuir isothermal biosorption parameters for the sorption of Cd(II) at 27^0C and pH 3 using maize leaf.

Freundlich parameters				Langmuir parameters			
1/n	K	R	S.D	b_m	Γ_m	R	S.D
0.8775	12.4462	0.9943	0.0275	10.179	-172.413	0.9869	0.0022

parameters compare well with those of other biosorbents that have been reported (Akar and Tunali, 2006). The values of the parameters show that maize leaf could serve as a good biosorbent for the uptake of Cd(II) from waste waters.

Figure 5 shows the variation of the removal efficiency with initial Cd(II) concentration. It is observed that increase in the initial Cd(II) concentration led to decrease in the removal efficiency due to saturation of the available binding sites on the maize leaf.

Thermodynamics of Cd(II) biosorption by maize leaf

The biosorption study can be regarded as a heterogenous and reversible process at equilibrium. The apparent equilibrium constant for the process has been shown (Han et al., 2005; Montanher et al., 2005) to be:

$$K_c = \frac{C_{ad}}{C_e} \quad \text{..........................(4)}$$

The Gibbs free energy of the biosorption process is thus given as:

$$\Delta G^0 = - RT\ln K_c \quad \text{....................(5)}$$

Where ΔG^0 is the standard Gibbs free energy change for the biosorption ($kJmol^{-1}$), R the universal gas constant ($8.314\ Jmol^{-1}K^{-1}$) and T the temperature (K).

The free energy change obtained for the biosorption of Cd(II) at 300K, initial Cd(II) concentration of 100 mgL^{-1} and pH 3 is –7.17 $kJmol^{-1}$. The large negative value of ΔG^0 obtained for the biosorption of Cd(II) shows the spontaneity of the biosorption process. The spontaneity observed for this study is more than twice what was reported for the biosorption of Pb (II) by waste beer yeast (Han et al., 2006) thus signifying that maize leaf could serve as biomass for biosorption of Cd (II).

Conclusions

This work suggests that the maize leaf could be used as an effective biosorbent for the treatment of Cd(II) bearing wastewater streams. The biosorption capacity was dependent on initial solution pH, contact time and the initial Cd(II) concentration. The maximum biosorption was obtained within 2 h at pH 3 and 300 K for initial Cd(II) concentration of 100 mgL^{-1}. The removal efficiency decreases with increase in initial Cd(II) concentration due to reduction in available binding site on the biosorbent for Cd(II).

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