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Full Length Research Paper

Thermodynamic and isothermal studies of the biosorption of cadmium (II) from solution by maize wrapper

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The removal of Cd (II) from dilute aqueous solution using maize (*Zea mays*) wrapper as a biosorbent was studied. The biosorption was pH-dependent with an optimum pH of 5 - 7. It was also time-dependent and maximum biosorption was obtained after 100 minutes. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherms. The Freundlich equation obtained was $\log \Gamma = 1.0813 \log C_e + 0.958$ while the Langmuir equation obtained was $^1/_\Gamma = 0.1535/C_e - 0.013$. The correlation factors were 0.99 and 0.99 while the standard deviation values were 0.051and 0.003 respectively. The free energy change obtained for the biosorption at 300 K, initial Cd (II) concentration of 100mg L^{-1} was –7.11kJmol^{-1}. These results indicate that maize wrapper has potential for the uptake of Cd (II) from industrial effluents.

Keywords: Biosorption, Cd (II), Freundlich isotherm, Langmuir isotherm, maize or wrapper.

INTRODUCTION

The removal of heavy metal ions from industrial waste-water using plant and animal materials is receiving much attention lately due to the relatively cheap cost of treatment. Different agricultural materials have been used in the biosorption of heavy metals from solution (Babarinde et al., 2006; Bayramoglu et al., 2006; Guibaud et al., 2006; Lu et al., 2006; Soliso et al., 2006; Babarinde et al., 2007). The potency of some plants materials to remove metals, which commonly occur in industrial effluents, has been studied. The effects of factors such as ionic strength, contact time, pH and initial metal ion concentration were investigated (Sawalha et al., 2006; Wang and Chen, 2006; Babarinde and Oyedipe, 2001; Babarinde et al., 2002; Babarinde, 2002; Akar and Tunali, 2006; Han et al., 2006). Materials of animal origin have equally been used (Vijayaraghavan et al., 2006). The choice of metals was made with regard to the industrial and potential pollution impact of cadmium.

Cadmium is one of the metals with the greatest potential hazard (Akar and Tunali, 2006). Maize wrapper was chosen as the biosorbent in this study because maize leaf from the same source has been reported to be effective in the biosorption of cadmium ions (Babarinde et al., 2007).

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MATERIALS AND METHODS

The maize (*Zea mays*) wrappers used as the biosorbent were obtained dry from a farm in Ijebu-Imushin, Ogun State, Nigeria. The dry wrappers were rinsed with distilled water, sun dried and cut into pieces of about 1 cm in length. They were kept in a dry place till the time of usage. Analytical grade $Cd(NO_3)_2.4H_2O$ was used for the preparation of stock solution. 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 dilution of the stock solution to the required concentrations. The initial pH of each of the solutions was adjusted to the optimum pH 7 by the addition of HNO_3 and/or NaOH solution, 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 for each biosorption study.

Biosorption studies

Each batch biosorption study was carried out by contacting the biomass with the solution in a glass tube under different conditions for a period of time. The uptake capacity of Cd(II) in batch system

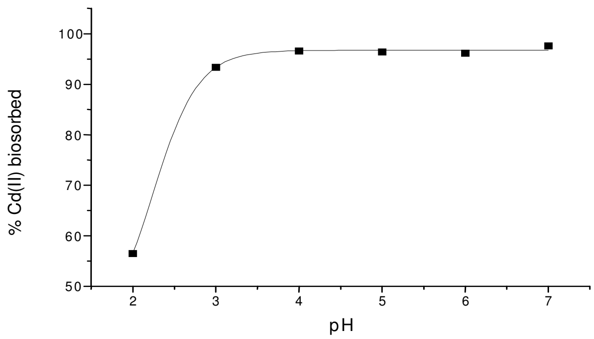

Figure 1. Effect of pH on the biosorption of Cd(II) by maize wrapper at 27˚C and initial metal ion concentration of 100 mg L^{-1}

was studied in a systematic way such that the effect of a parameter was monitored while other parameters are kept constant. Studies on the effect of solution pH, contact time, and initial metal ion concentration on the biosorption of Cd(II) were conducted at 27°C in a thermostated water bath (Haake Wia Model). The current generated by the pumping in the water bath provided the agitation needed to attain equilibrium. The biomass was separated from the sorbate solution by filtration. The residual metal ions were analyzed using an 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. The removal efficiency of the Cd(II) was calculated as:

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

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

Effect of pH on biosorption

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) 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 ad 1 – 7.5, respectively. The procedure used is similar to those earlier reported (Vasuderan et al., 2003; Xu et al., 2006 and Babarinde et al., 2006). Studies were conducted at 27°C to study the effect of initial solution pH on the biosorption of Cd(II) by contacting 0.5 g of the maize wrapper with 50 ml of 100mgL^{-1} Cd(II) solution in a glass tube. The pH of each of the solutions was adjusted to the desired value with 0.1M HNO_3 and/ or 0.1M NaOH.

The studies were conducted at pH 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 filtration and the residual Cd(II) concentration in the solution was analyzed. Each of the studies was conducted in triplicates and the mean value was determined for each pH. Subsequent biosorption studies were performed at pH 7.

Effect of contact time on biosorption

The biosorption of Cd(II) by maize wrapper was studied at various time intervals (0 – 120 min. A constant concentration of 100mgL^{-1} was used. 0.5 g of maize wrapper was weighed into each glass tube and 50 ml of Cd(II) solution at pH 7 introduced into it.

Effect of initial Cd(II) concentration on biosorption

Batch biosorption study was carried out using a concentration range of 10 – 100 mgL^{-1}. 0.5 g of the maize wrapper was introduced into each of the glass tubes employed and 50 ml of Cd(II) solution at pH 7 was added to the tubes. Three glass tubes were used for each concentration. The biosorption mixture was then left in a thermostated water bath to maintain the temperature of 27°C for optimum contact time required to reach equilibrium time. The maize wrapper was removed from the solution and the concentration of residual Cd(II) in each solution was determined.

The results obtained were analyzed using both Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) isotherms. The linear form of the Freundlich isotherm is

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

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

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

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

RESULTS AND DISCUSSION

Effect of solution pH on biosorption

The result of the pH study is shown in Figure 1. The result shows that maximum biosorption was obtained at pH 5 - 7. The percentage Cd(II) biosorbed is slightly lower at lower pH values. This result confirms the earlier report that the biosorption is pH-dependent (Pavasant et al., 2006). The result suggests that optimum biosorption is obtained at pH 5 - 7 and that initial pH would play a vital role in the removal of the Cd(II) from aqueous solution using maize wrapper.

Effect of contact time on 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 biosorptive capacity of 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 reached equilibrium within 100 min as the binding sites on the biomass were used up. The period of 100 min was therefore used for the biosorption of Cd(II) by maize wrapper. The 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 metal biosorption rate is high at the beginning but plateau values were obtained in 100 min, similar to what was reported by Liu and co-

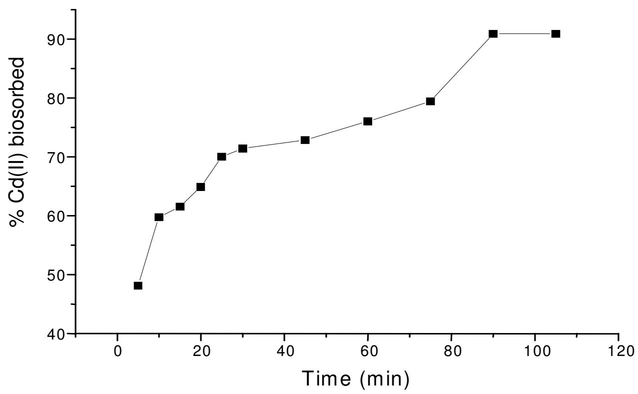

Figure 2. Time course of the biosorption of Cd(II) by maize wrapper at 27°C, pH 7 and initial metal ion concentration of 100 mg L^{-1}

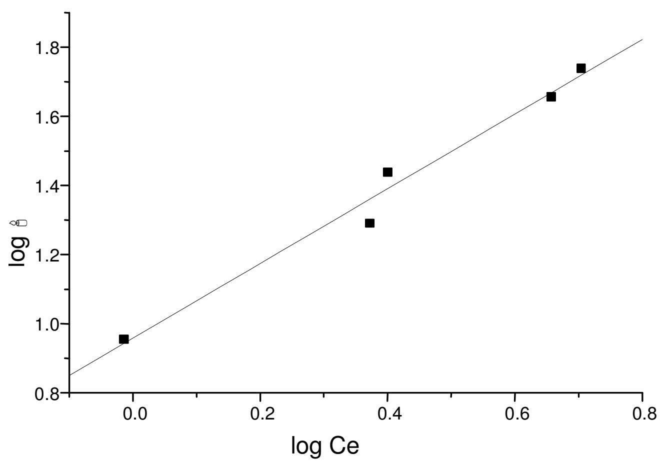

Figure 3. Freundlich Isotherm for the biosorption of Cd(II) ion using maize wrapper at 27°C, pH 7 and initial metal ion concentration of 100 mg L^{-1}

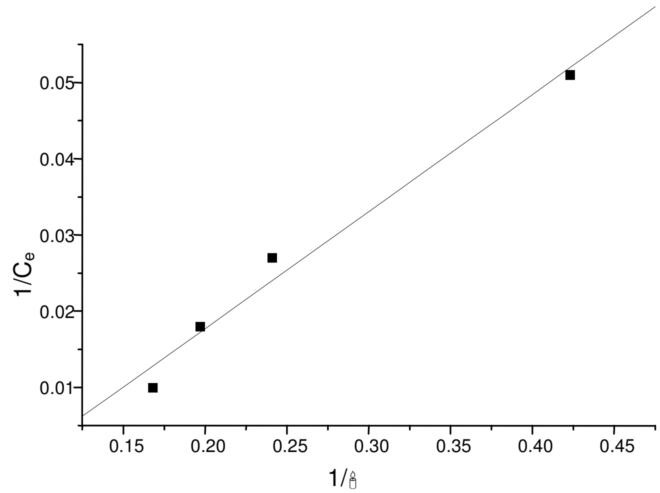

Figure 4. Langmuir Isotherm for Cd(II) by maize wrapper at 27°C, pH 7 and initial metal ion concentration of 100 mg L^{-1}.

workers (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 the metal ion was biosorbed at the initial metal ion concentration of 100 mgL^{-1} within the first 100 min. The efficiency increases as the initial metal ion concentration increases. The gradual increase in the efficiency of the biomass shows nearness to saturation of the available binding sites on it. The same experimental data were applied to both the Freundlich and Langmuir isotherm models as shown in Figure 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 parameters compare well with those of other biosorbents that have been reported (Akar and Tunali, 2006; Han et al., 2006; Sathinshkumar et al., 2007). The values of the parameters show that maize wrapper is a good biosorbent for the uptake of Cd(II) from waste waters.

Thermodynamics of Cd(II) biosorption by maize wrapper

The biosorption experiment 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:

$$K_c = \frac{C_{ad}}{C_e} \qquad (4)$$

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

$$\Delta G^0 = - RT\ln K_c \qquad (5)$$

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 300 K, initial Cd(II) concentration of 100 mg L^{-1} and pH 7 is –7.11$kJmol^{-1}$. 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 2 times what was reported for the biosorption of Pb(II) and more than seven times what was reported for the biosorption of Cu(II) by waste beer yeast (Han et al., 2006). This implies that maize wrapper is an excellent biomass for the biosorption of Cd(II).

Table 1. Freundlich and Langmuir isothermal biosorption parameters for the sorption of Cd(II) at 27°C and pH 7 using maize wrapper.

Freundlich parameters				Langmuir parameters			
1/n	K	R	S.D	b_m	Γ_m	R	S.D
1.0813	9.0782	0.99	0.051	6.5147	-76.92	0.99	0.003

Conclusion

Biosorption studies performed on the maize wrapper to remove cadmium ions from aqueous solution showed quantitative removal at lower pH values. Batch studies show that the biosorption is pH, time and concentration dependent. The process reached equilibrium in 100min and the optimum pH is 5 - 7. Increasing the initial concentration of Cd(II) results in higher adsorptive quantity. The experimental data of biosorbing Cd(II) fit well to Freundlich and Langmuir model equations. The process is thermodynamically spontaneous and the biosorbent is better than some of those already reported.

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