COMPARISION OF DIFFERENT COLUMN STUDY FOR REMOVAL OF HEAVY METAL

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Abstract

This work reports great efficacy of *Tinospora cordifolia* as biosorbent for removing cadmium ions from synthetic and industrial solutions. The highest ever reported biosorption capacity was obtained under optimal conditions. The scope of work included uptake capacity, equilibrium study and column study at varying pH , contact time , biosorbent dose, initial metal concentration. The absorption equilibrium was attained in a very short time (5 minutes). Both Langmuir and Freundlich isotherm model were applied to study the dose-response behavior and it was observed that the Freundlich model provided a high R^2value. The FTIR analysis indicated involvement of hydroxyl, alkane, anhydride, halide and amine functional groups. Increase in pH after adsorption is a further corroborative proof. The biomass was successfully applied for the removal of cadmium from industrial effluents. The feasibility and viability of the biomass for techno-commercial utilization appears high.

Keywords: biosorption, biomaterial, cadmium, column mode removal, Fourier Transform Infrared

INTRODUCTION

Cadmium is ubiquitously present as an impurity in sulphide ores or native deposit. The greatest use of cadmium is primarily for metal plating and coating operations, including transportation equipment, machinery and baking enamels, photography and television phosphors. It is also used in nickel-cadmium and solar batteries and in pigments. Cadmium and its compounds are extremely toxic even in low concentrations, and they accumulate in organisms and ecosystems. Cadmium has no constructive purpose in the human body (Tilaki et al. 2004). Workers exposed to high background levels of cadmium in industrial situations may have an increased risk of cancer. Cadmium is reported to potentially cause a variety of effects from acute exposures, including: nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure etc. Cadmium has the chronic potential to cause kidney, liver, bone and blood damage from long term exposure. World Health Organization has recommended the permissible limit of cadmium 0.005 mg/L in water. The methods like ultra filtration, RO membranes, sonoelectrolysis, precipitation, etc. for the removal of heavy metals are quite costly. These processes produce large quantity of sludge which when disposed to environment can cause even more acute problems. Compared to them the

biosorption process offers potential advantages such as low operating cost, minimization of chemical and biological sludge, high efficiency of heavy metal removal from dilute solutions and environmental friendly (Ahluwalia and Goyal 2007).
The present research work was aimed at finding biomaterial with high capacity of cadmium adsorption. Series of experiments were conducted with many locally available biomaterials. Finally the most promising biomaterial was subjected to variety of expedients viz. the influence of contact time, solution concentration, dose of biomass and solution pH of biosorption of cadmium etc. The Langmuir and Freundlich isotherm models were used for the mathematical description of the biosorption equilibrium. The column study and FTIR analysis were also carried out.

MATERIAL AND METHODS

Batch Mode Adsorption Study

Batch mode of adsorption study was carried out to characterize the binding of metal with the active sites of the biomass. Different concentration of cadmium (5-1000-ppm) was prepared in 50 ml of distilled water. The pH of the solution was maintained at 5. The experiment was performed by mixing definite quantity of biomass. The reaction mixture was agitated for 30 minutes at room temperature 28 to 35^0C. Similarly the control sample was prepared. After this period solution was filtered with membrane filter and analyzed for the concentration of the cadmium remaining in the solution by fast sequential atomic absorption spectrometer (AA240FS, Varian). Further the effect of various parameters such as pH, biomass dose, concentration and contact time were carried out.

Column Mode Adsorption Study

Column mode study was performed for the adsorption of cadmium by the biomass. Analytical grade of cadmium stock solutions at 1000 mg/l were used for the study. The column was charged with Cadmium bearing water in the up flow mode with a flow rate of 13 ml/minute. The flow rate was maintained by using peristaltic pump. The inflow pH was 5 for all studies. This was in accordance with the earlier study (Mehmet et al. 2007). The initial concentration of Cadmium was 100-ppm. Effluents were collected at regular time interval and were analyzed by Fast sequential atomic absorption spectrometer (AA240FS, Varian), to determine the retention capacity of biomass.

RESULTS AND DISCUSSIONS

The new biomass has been found to possess excellent biosorptive capacity for the cadmium. The range of various parameters for optimum performance is reported here.

Effect of pH on Biosorption

Batch pH experiment was carried out to see the effect of pH at a range from 1-8. The pH profile showed an increase in metal uptake from 45% to 98% on increasing the pH 1-3 at 100-ppm cadmium concentration, 5 gram biomass and a contact time of 30 minute. A constant adsorption of about 98% was observed from pH 3 to pH 8. The further increase in pH beyond 8 caused a decrease in the adsorption of cadmium. This trend can be explained based on the behavior of Cd(II) in the aqueous system. For the $CdCl_2$ system Cd^{2+} was the dominant species up to pH 8 and was strongly adsorbed by biomass. However, above pH 8 the $Cd(OH)_2$ becomes the dominant species which starts to precipitates in the manner concomitant with the increasing pH (Baes and Mesmer 1976). On the other hand the low pH i.e. higher H+ concentration of the solution had shown diminished adsorption of cadmium to the biomass, obviously due to the higher presence of competing ions. This explanation was confirmed by the adsorptive behavior at pH 8 when such an increase in pH was not observed (Pandey and Chandrashekhar 2008).

Effect of biosorbent dose

The effect of adsorbent dose on the removal of Cadmium was studied by varying the dose of adsorbent from 1 to 8 gm. The percentage removal increases from 72 to 99% by increasing the adsorbent dosage from 1 to 5 gm. However, the adsorption capacity showed a constant trend with increasing biomass dosage. This increasing of adsorption is due to the increased availability of active adsorption sites arising due to the increase in dose of adsorbent. The optimum biomass dose was considered to be 5 gm.

Effect of Contact Time on Biosorption

This biomass show very high capacity Cadmium adsorption within 5 minute i.e. above 95% and reaches to above 98% as contact time increases up to 30 minute. A further increase in contact time has a negligible effect on the percentage removal. The fast initial metal biosorption rate was attributed to the surface binding and the following slower sorption was attributed to the interior penetrate (Lodi et al. 1998). The active binding groups with higher affinities are firstly occupied (Chojnacka et al. 2005). The optimum contact time for the removal of Cadmium by biomass is 30 minute.

Metal binding capacity of biomass

For the determination of uptake capacity and the effect of increasing metal ion concentration on biosorption the experiments were conducted at the optimum determined pH of 5. After an equilibrium period of half an hour, the supernatant was analyzed for the unadsorbed cadmium. The result showed a complete removal of 100-ppm cadmium. With the further increase in the initial cadmium concentration, the percentage removal was found to reduce to 5% for 1000-ppm. This decrease can be attributed to the non-availability of any more active sites.

Analysis of the Kinetic of Cadmium removal

The amount of metal ions adsorbed at equilibrium, qe (mg/g), was calculated as

$$Qe = (Co-Ce)\ V/W$$

Where Co and Ce are concentrations (mg/L) of metal ions in the initial and equilibrium solutions, respectively, V is volume (L) of the initial solution taken for equilibration, W(g) is the weight of the pellets taken for equilibrium.

Experimental results obtained for adsobtion of metal ions at equilibrium were analyzed by both the Freundlich & Langmuir adsorbtion isotherm. The Freundlich isotherm is described by,

$$Qe = KFCe1/n$$

Where KF is a constant related to the adsorption capacity and n is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. Adsorbtion is Favourable for values $0.1 < 1/n < 1$ (Rajji and Anirudhan 1998).

Both Langmuir and Freundlich isotherm models explained adsorption of heavy metals shown in Fig.1& 2. The data fitted well in Freundlich adsorption isotherm as compared to Langmuir isotherm.

Fourier Transform Infrared Spectrometer (FTIR) spectral study

FTIR analysis of unloaded biomass displayed a number of absorption peaks, indicating the nature of biomass examined.Results of FTIR analysis of native and cadmium loaded biomass are shown in Fig. 3 & 4 and by Table.1. The peak observed at 3427.4 cm-1 of alcohol is shifted to 3448.7 cm-1 so here some alteration in OH stretch is observed i.e. peak become sharp which is due to the occupation of ligand metal atom of cadmium. Peak at 1429.3 cm-1, 1375.8 cm-1, 1326.9 cm-1, 1258.8 of unloaded biomass is disappear in FTIR of loaded cadmium biomass, here saturation of bond may can be form due to the occupation of ligand atom of cadmium after adsorption.

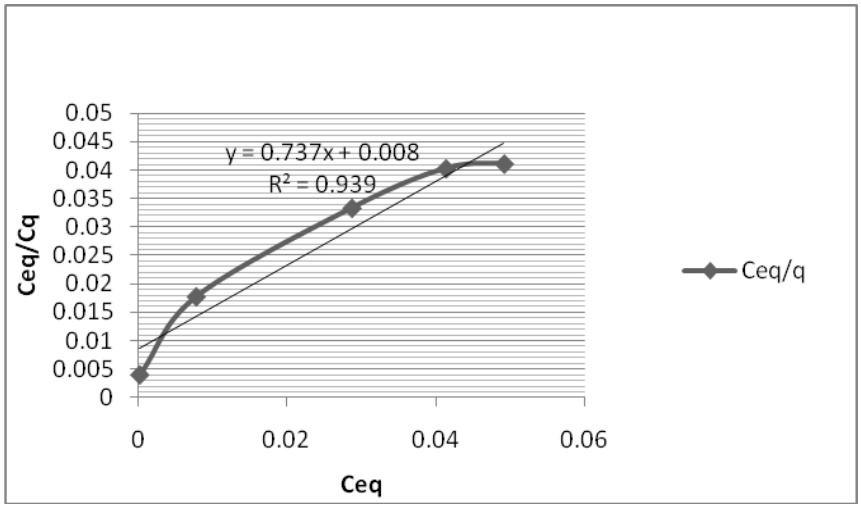

Fig.1. Langmuir isotherm depicting the adsorptive behavior of Cd

Column Study

Column experiment was performed in order to evaluate the removal and recovery of cadmium under flow conditions. Continuous mode analysis (column study) was performed in order to make use of biomass for large scale treatment of cadmium contaminated water. Column study was performed to determine the break through curve. The break through curve as shown in Fig.5 indicates the complete removal of 100-ppm cadmium up to 5.65 liter. The biomass was completely exhausted by after the inflow of 61.7 liter of 100-ppm synthetic Cadmium solution as shown in Fig.6. The EBCT (Empty bed contact time) was calculated by

EBCT = 1 Bed volume / Flow rate

Here firstly bed volume is calculated by formula given below

Bed volume = πr2l

EBCT was found to be 477.71ml.

61.7 liter of synthetic cadmium solution was pumped into the column to exhaust the biomass in column mode with the value of bed volume and flow rate, EBCT was calculated. Removal capacity of the biomass was calculate by the following equation

Removal capacity = CI –CF/M * V

Whereas CI is initial metal concentration (ppm), CF is final metal concentration (ppm), v is volume of solution (l) and M is the mass of the sample (gm). It was found to be 11.07g/g.

CONCLUSION

The research work deals with the search of highly efficient biomass for biosorption of cadmium in wastewater. The optimum parameters like dose of biomass, pH, contact time and concentration of solution were studied. The maximum adsorption capacity of biomass was found to be 3.9 g/g upto 1000-ppm. After adsorption, the pH of the test water sample increases between 6 and 7. Thus the biomass is effective in decreasing the acidity of the water sample. It is suitable only for cadmium contaminated water. In the presence of other co-ions the increase in pH is not very significant. The adsorption isotherm found to be well fitted by both Langmuir and Freundlich

equation. The breakthrough and exhaust point in column study was found to be 5.45 L and 61.7 L respectively. Column type biosorption was more efficient as compared to batch mode adsorption study because of more close packing of adsorbent sites. The biomass was effectively used for the removal of cadmium in industrial wastewater.

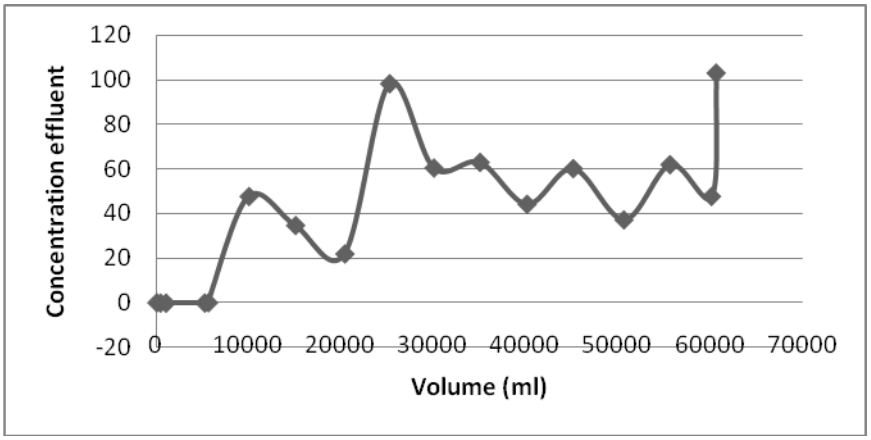

Fig.2. Exhaust curve for removal of Cd in column mode
(Influent Cd Concentration: 100 mg/L)

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