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Biosorption Studies for Removal of Cadmium from Wastewater using Immobilized *Saccharomyces cerevisiae*

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Biosorption process has been proposed as an efficient, potential, cost effective way of removing toxic metals from industrial effluents at low concentration of below 100 ppm. In the present study a new biosorbent material a waste product from breweries containing yeast, *Saccharomyces cerevisiae*, was immobilized and was used as an absorbent for removal of cadmium, as yeasts are capable of accumulating various heavy metals. Studies on the removal of cadmium from aqueous solutions using *Saccharomyces cerevisiae* immobilized in 4% sodium alginate beads were undertaken. Adsorption was carried out using free cells, immobilized beads in presence and absence of biomass. The results indicate that the amount of cadmium adsorbed increases with increase in metal concentration and decreased with decrease in pH. Increase in sodium alginate concentration increased in the metal adsorption. The equilibrium data was fitted to Freundlich type of equation in all cases of present study. Finally an empirical correlation was proposed to estimate the equilibrium distribution of cadmium between immobilized biomass and aqueous solution.

Key Words: Biosorption, Cadmium removal, Immobilized yeast.

INTRODUCTION

Metallurigical industries produce large volumes of effluents especially as aqueous discharge, which are harmful to mankind. Heavy metal ions are indeed the key role players of pollution, which diversify into ecological alterations. Cadmium is one of such heavy metals that is toxic and harmful to mankind and needs to be removed from waste liquors. Biosorption, which is defined as the accumulation and concentration of pollutants from aqueous solutions and the method is feasible and economically viable attractive approach[1]. Biosorption is a process that utilizes inexpensive biomass to sequester toxic heavy metals and is specifically useful for the removal of contaminants from industrial effluents.

Many processes have been used for the removal of heavy metals from industrial effluents *viz.*, chemical precipitation, coagulation, solvent extraction, membrane separation, ion exchange, reverse osmosis and adsorption[2]. Compared with the conventional methods for removing toxic metals from industrial effluents, the biosorption proces offers several advantages, such as low operating cost, minimization of the volume of biological sludge to be dispersed of, high efficiency in detoxifying very dilute effluents and no nutrient requirements[3]. Bioremediation is suggested to be eco-friendly and cost effective technology as compared to chemical techniques like precipitation, ion-exchange and membrance processes[4]. Cadmium can cause problem such as hypertension emphysema, renal cancer and prostrate cancer and kidney disease. Rostami *et* al[5] studied the cadmium adsorption on the fungal biomas *i.e. A. niger*, *P. austurianum* and the data were fitted to Frendlich and Longmuir models. Immobilization of yeast[6] cells were effective bioaccumulators for removal/recovery of cadmium from synthetic solutions. The Freundlich[7] and Longmuir[8] models were applied for estimation of maxiumum cadmium uptake by the biomass. In biosorption, negatively charged ionic groups on microbial surfaces sequestered the positively charged heavy metal ions. These microbial surfaces may be polysaccharide capsules, slime layers of other binding sites such as carboxyl, phosphate residues, S-H groups and hydroxyl groups[9-11]. In view of the above the present work is directed to study the removal of cadmium using *Saccharomyces cerevisiae* using biosorption technique.

EXPERIMENTAL

All the chemicals used are of A.R. grade supplied by either Qualigens or Loba. A new biosorbent yeast *Saccharomyces cerevisiae* was collected from G.M.R. Breweries Ltd., Ranastalam, Srikakulam, India.

Immobilization: 4 g of sodium alignate was dissolved in hot water and stirred vigorously with magnetic stirrer for 10 min to obtain a thick uniform solution. 1 g of dead biomass was stirred vigorously for 15 min to get uniform suspension of biomass throughout the sodium alginate solution. This mixture was filled into the burette and dropped into the beaker, containing 0.05M $CaCl_2 \cdot 2H_2O$ to obtain the beads. These beads were stored in 0.025 M solution of $CaCl_2 \cdot 2H_2O$.

Procedure: 100 mL of cadmium solution of known concentration was taken in a 250 mL conical flask and 25 mL of immobilized beads were added. The flask was shaken for the desired time using orbital shaker. The samples were collected and analyzed for metal concentration using atomic absorption spectrophotometer of Perkin-Elmer model 3100. The required pH was adjusted by adding hydrochloric acid to the aqueous solution.

RESULTS AND DISCUSSION

100 mL of aqueous solution containing cadmium and 1 g of free cells of *Saccharomyces cerevisiae* were taken in stoppered conical flasks and were shaken using an orbital shaker. The samples were withdrawn at regular intervals of time to determine the time required to attain equilibrium. Fig. 1 shows the variation of aqueous metal concentration with time. This data showed that the aqueous metal concentration decreased with increasing time and reached a plateau, indicating the attainment of equilibrium. It showed that the system has approached equilibrium in less than 3 h. Hence all the subsequent experiments were conducted for a period of 3 h in order to ensure the attainment of equilibrium.

Studies using free cells

Effect of pH: Fig. 2 shows the variation of C_S (mg of cadmium adsorbed/g of free cells) with C_A (aqueous metal concentration, ppm) at diferent pH values. It was observed that the increase in aqueous metal concentration increased metal adsorption. It was also found that the decrease in pH dcreased metal adsorption. This may be due to adsorption of H^+ at low pH values.

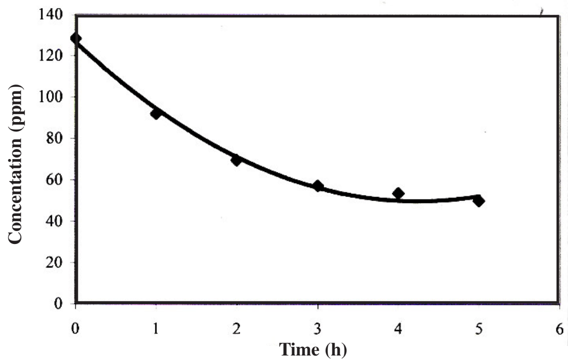

Fig. 1. Variation of aqueous metal concentration with time

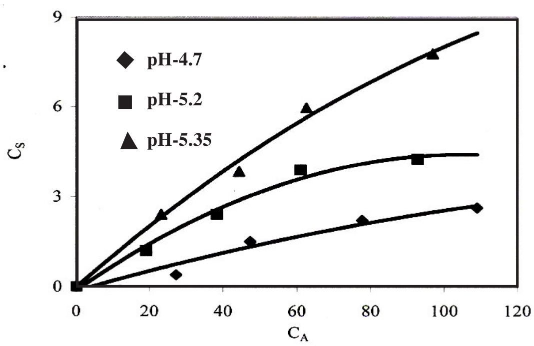

Fig. 2. Effect of pH on equilibrium adsorption of cadmium over free cells

Effect of particle size: Variation of metal adsorption on free biomass with aqueous metal concentration is plotted in Fig. 3 for different sizes of biomass particles covered in the present study (-44 + 72; -72 + 150; -150 + 200). The particle size exhibit negligible effect on the adsorption of cadmium.

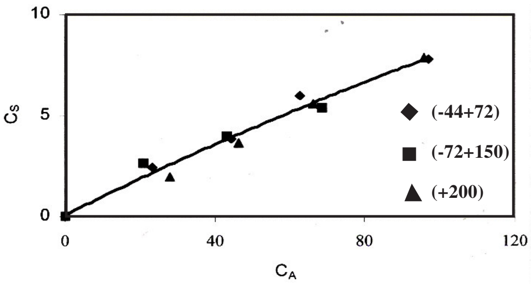

Fig. 3. Effect of particle size on equilibrium adsorption of cadmium over free cells

Studies using immobilized beads

Adsorption over alignate beads without biomass: Experiments were conducted to study the adsorption capacity of calcium alginate beads in absence of any biomass. Fig. 4 showed the variation of metal adsorbed (C_S) in the aqueous phase (C_A) at different pH values. It was found that pH had little effect within the range covered in the present study.

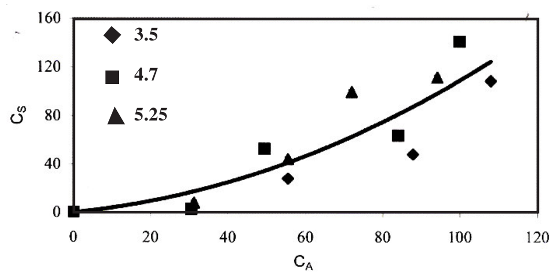

Fig. 4. Effect of pH on equilibrium adsorption of cadmium over beads in absence of biomass

Effect of alginate concentration on adsorption in presence of biomass: The sodium alginate concentration is expected to affect metal adsorption. Fig.5 shows that the increase in sodium alginate concentration increased metal adsorption. Further, it is seen that the increase in the range of 1-2% was more pronounced in comparison of the concentration in the range 2-4%. Further it was found that the effect was more pronounced at higher metal concentrations than lower metal concentrations.

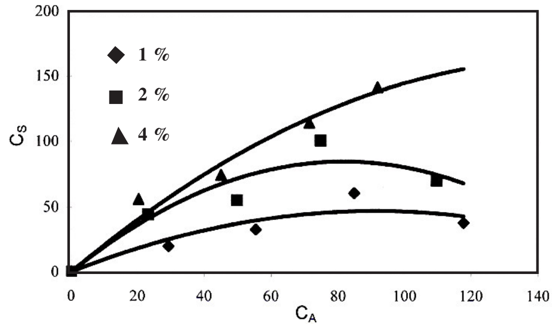

Fig. 5. Variation of aqueous metal concentration with different alginate per cent over beads in presence of biomass

Comparison of free and immobilized cells: The adsorption data on cadmium over free biomass and immobilized alginate beads in presence and absence of biomass is shown in Fig. 6. The metal adsorption in immobilized biomass beads was found to be very much higher than that in free cells as well as sodium alginate beads in absence of biomass. This indicates that the immobilized biomass beads are superior for cadmium uptake, besides it has the advantage of reusabiilty.

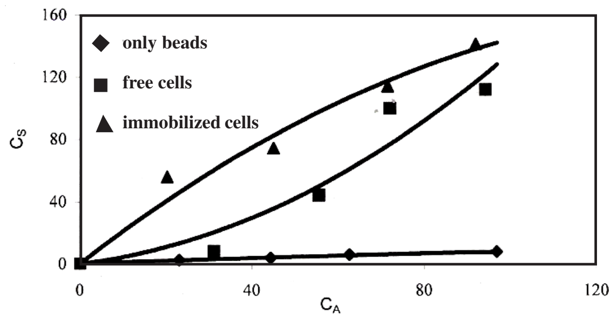

Fig. 6. Comparison of metal adsorption over free cells, beads in presence and absence of biomass

Correlation of results: The equilibrium distribution data were shown in Figs. 7, 9, 10 and 12 on log coordinates for different conditions of present study. In all cases the data are fitted to straight lines indicating the validity of Freundlich type of equation for the adsorption data.

Adsorption on free biomass: Fig.7 shows that the variation of log C_S (mg of cadmium adsorbed/g of free cells) with log C_A (aqueous metal concentration, ppm) at different pH values. The data are found to fit into a straight line, for all pH values. The slopes of these lines are approximately the same but the intercepts varied. Hence the variation of C_S and C_A is given by

$$C_S \propto C_A^{0.816}$$

$$C_S = K.C_A^{0.816} \quad (1)$$

where the proportionality constant K is a function of pH. The intercepts (log K) were shown against pH in Fig.8. The resulting straight line can be represented by the following equation:

$$\log K = I = 0.3417\ pH - 2.6598$$

$$K = 0.00219 C_H^{-0.3417} \quad (2)$$

combining equations (1) and (2)

$$C_{S,fc} = 2.19 \times 10^{-3}\ C_H^{-0.3417} C_A^{0.816}$$

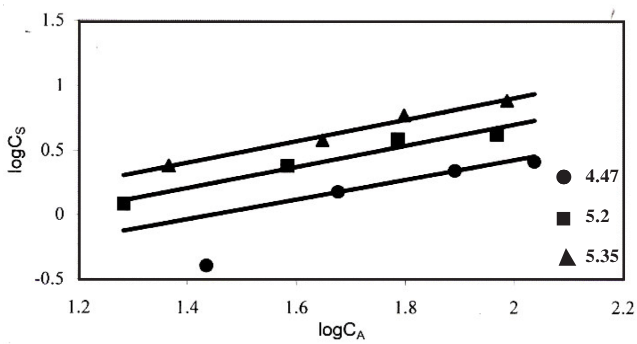

Fig. 7. Freundlich plot at different pH values for adsorption of cadmium over free cells

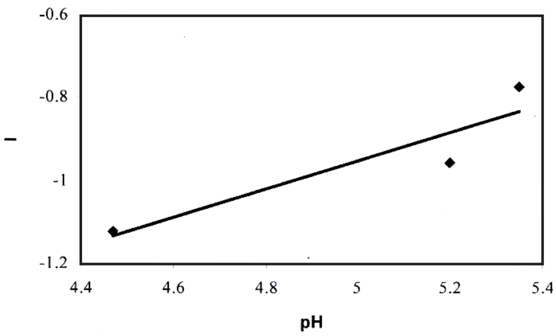

Fig. 8. Variation of intercept I, with pH in presence of free cells

Adsorption on sodium alginate beads in absence of biomass: Fig. 9 shows the variation of metal concentration in the solid beads with that in the aqueous solution at different pH values on log coordinates. The pH showed negligible effect on equilibrium distribution. The data are fitted to a straight line showing the applicability of Freundlich equation. The straight line can be represented by the following equation:

$$C_S = 1.29 \times 10^{-4}\ C_A^{3.024}$$

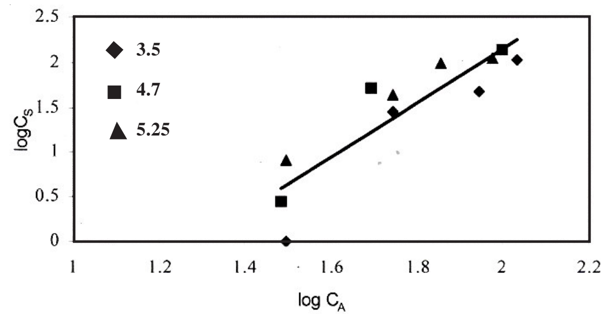

Fig. 9. Freundlich plot at different pH values for adsorption of cadmium over beads in absence of biomass

Adsorption on immobilized of biomass beads: Fig. 10 shows the reundlich plot for cadmium adsorption over immobilized alginate beads for different concentrations of sodium alginate (1, 2, 4 %). The data have been fitted to straight line of slope 0.6259 in all cases. The data can be represented by the following equation

$$C_{S,IB} \propto C_A^{0.6259}$$

$$C_{S,IB} = K'C_A^{0.6259} \quad (3)$$

where K' varies with sodium alginate concentration.

Fig.11 shows variation of K' with sodium alginate concentration expressed in weight per cent on log coordinates and the resulting straight line can be represented by the equation

$$\log K' = I' = 0.7584 \log C_X + 0.4695$$

where C_X is the alginate concentration.

$$K' = 2.948\ C_X^{0.7584} \quad (4)$$

combining equations (3) and (4)

$$C_{S,IB} = 0.3392\ C_X^{0.7584} C_A^{0.626}$$

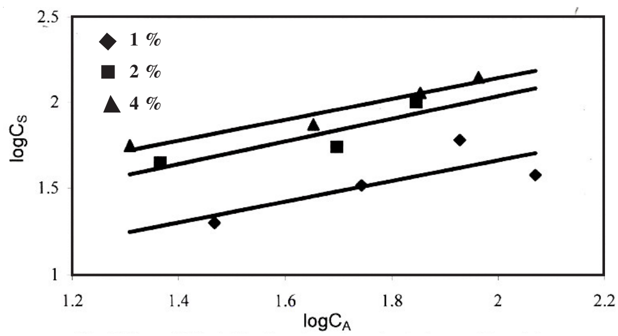

Fig. 10. Freundlich plot for the adsorption of cadmium over beads in presence of biomass with different alginate concentration in wt. %

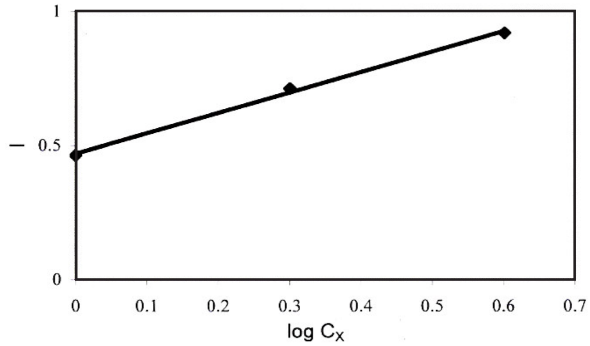

Fig. 11. Variation of intercept I, with alginte concentration in wt. %

Fig. 12 shows that pH had negligible effect on equilibrium distribution within the range of present study.

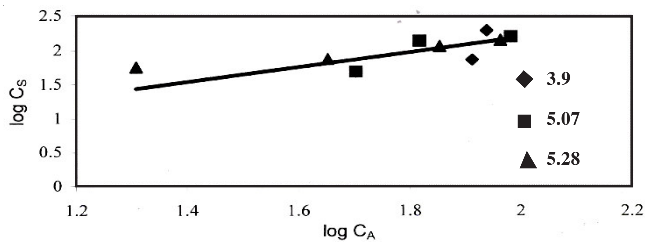

Fig. 12. Freundlich plot at different pH values for adsorption of cadmium over immobilized cells

Alternatively the data are subjected to regression analysis and the following equations were obtained

For free cells $C_{S,FC} = 0.0002155\ C_H^{-0.5228} C_A^{0.8718}$

For immobilized cells $C_{S,IB} = 2.426\ C_X^{0.7116} C_A^{0.6892}$

The abvoe equations fit the data very well with an average deviation of 12 and 15 %, respectively and are comparable to those obtained by graphical analysis.

Conclusion

The spent yeast *i.e. Saccharomyces cerevisiae* from a wine manufacturing company can be used to remove cadmium from wastewaters by biosorption technique. Decrease in pH results in decrease in the metal adsorption in case of free cells while pH had marginal effect when using immobilized cells. The metal adsorption over immobilized biomass was found to be higher when compared to that on either free cells or immobilized beads without biomass. The Freundlich type equation has represented the data satisfactorily.

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