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Biosorption of Zn (II) ions from Aqueous Solution by Immobilized *Aspergillus fumigatus*

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ABSTRACT: The objective of this study was to investigate the biosorption of Zn (II) from aqueous solution by *Aspergillus fumigatus* immobilized in calcium alginate. The effects of adsorbent dosage, initial solution pH, contact time and initial Zn (II) concentrations were investigated. Results were fitted to the Langmuir isotherm. The results showed an increase in biosorption efficiency with increase in biosorbent dosage. The optimum pH of adsorption was 5.0 while the maximum adsorption was achieved within 10 minutes at initial Zn (II) concentration of 1 mg/L. The experimental results showed a high R^2 (0.9070) value for the Langmuir isotherm. This therefore suggests that it is a monolayer adsorption. The maximum biosorption capacity was 3.55 mgg^{-1}. These results indicate that zinc metal removal by biomass of *Aspergillus fumigatus* immobilized in alginate is a low cost wastewater treatment option and can be effectively used in small scale treatment plants.

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Heavy metal ions can be discharged into the environment from a variety of industrial activities (Cem and Aytas, 2009). They tend to persist and accumulate in every part of the food chain (Vijaya *et al*., 2008). The removal of these metals from industrial wastewaters is a problem of increasing concern that has been mostly solved by chemical and physical methods of treatment. (Ahalya *et al*., 2003). These methods are however expensive and sometimes generate undesirable by-products. Biosorption is therefore seen as an alternative method that can be categorized as a green technology for heavy metal removal from industrial effluents (Wang and Chen, 2009). Biosorption is a term that describes the removal of heavy metals by passive binding to non-living biomass from an aqueous solution (Davis *et al*., 2003).

The process has gained importance due to its advantages over the conventional removal techniques. These advantages include the reusability of the biomaterial, low operating cost, improved selectivity for specific metals of interest, short operation time and non-production of secondary compounds which might be toxic (Spinti *et al*., 1995). This study has been carried to investigate the capacity of the fungus *Aspergillus fumigatus*, immobilized in calcium alginate, to adsorb Zinc (II) ions from aqueous solution and to determine the optimization parameters for the process.

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MATERIALS AND METHODS

1000 mg/L solution Zn (II) metal solution was prepared by dissolving 2.092 g of $ZnC1_2$ in a small volume of distilled water in a 1 dm^3 volumetric flask and made up to the mark with more water. The fungal mycelia of *Aspergillus fumigatus* was cultured over Potato Dextrose Agar (PDA) plates. The PDA plates of the stock culture were maintained by subculturing at 4 ^oC. The fungal biomass was cultivated in composition (g/L): K_2HPO_4, 0.5; NaCl, 0.5; $MgSO_4$, 0.5; NH_4NO_3, 0,5; yeast extract, 0.5, peptone, 10.0, glucose, 20. The pH of the media was adjusted to 5.0. The flask was autoclaved at 121 ^oC for 15 minutes and then incubated in a rotary orbital shaker at 180 rpm and 30 ^oC. It was dried at 80 ^oC overnight and was subsequently used for all the experiments (Pundir and Dastidar, 2010).

100 ml of 4 % (w/v) sodium alginate was mixed until homogenous with 2% (w/v) solution of the fungal biomass. The mixture was stirred for 1 hour at 30^oC and then the slurry was dropped through a 10 ml syringe into 2% (w/v) $CaCl_2$ solution (Dong, 2004). Durable spherical beads containing the biomass were formed immediately. The beads were washed with distilled water and stored at 4 ^oC in distilled water until further use. The adsorption experiments were carried out by varying one parameter at a time while keeping the others constant. The parameters investigated were

effects of adsorbent dosage, solution initial pH, initial metal ion concentration and contact time. The experiments were carried out in 100 ml conical flasks containing 50 ml of solution at a constant temperature of 29 °C. The samples were agitated on a conical flask shaker at 150 rpm at the stated conditions. After equilibrium was attained, the samples were filtered into polypropylene bottles using Whatman No1 filter paper. The residual concentrations of the Zn (II) ions were determined using an Atomic Absorption Spectrophotometer (AAS). The percentage metal removal (%) was calculated using the following equation:

$$\text{Removal } \% = \frac{(C_o - C_e)}{C_o} \; x\; 100 \quad .....(1)$$

Where C_o and C_e are the initial and the residual (equilibrium) concentrations in mg/L, respectively. The amount of Zn (II) ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation below (Babel and Opiso, 2007):

$$q_e = \frac{V(C_o - C_e)}{M} \quad ....(2)$$

Where q_e is the amount adsorbed in mg/g of the absorbent at equilibrium, C_o and C_e are the initial and the equilibrium concentrations in mg/L, respectively, V is the volume in litres of the solution used during the experiment and M is the mass of the adsorbent in grams.

The Langmuir adsorption isotherm is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is expressed by the equation below.

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \quad ....(3)$$

Where K_L (L/g) is a constant related to the adsorption / desorption energy and Q^o (mg/g) is the maximum sorption upon complete saturation of the adsorption of the adsorbent (biosorbent) surface (Horsfall *et al*., 2004). A graph of C_e/q_e against C_e will have K_L (L/g) as the slope and Q^o (mg/g) as the intercept.

RESULTS AND DISCUSSION

Effect of adsorbents dosage on percentage removal of Zn (II) was investigated by varying the adsorbent dosage from 10 mg to 200 mg while keeping the other parameters constant. The result is presented in Fig 1. The highest percentage removal of 97.26% was achieved at 150 mg biomass weight after which there was no further increase. The increase in percentage removal of Zn (II) with increase in adsorbent dosage is due to the fact with increase in adsorbent dosage, more and more surface becomes available for solutes to adsorb and this increases the rate of biosorption. When an optimum amount has been adsorbed, the rate of biosorption decreases and desorption comes into play which considerably reduces the overall rate of removal. The adsorbed ions either block the access to initial pores or cause particles to aggregate, thereby reducing the active site availability (Garg *et al.*, 2004).

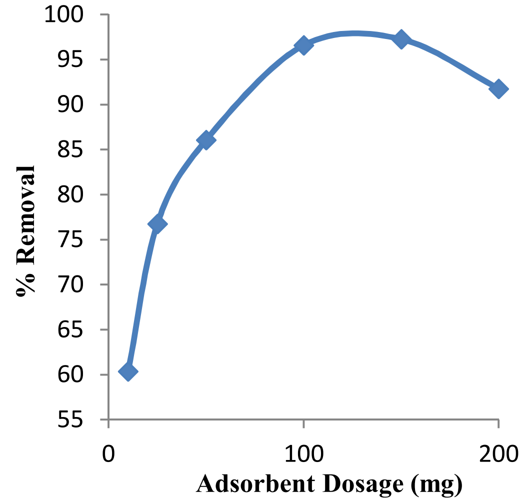

Fig 1 Effect of adsorbent dosage on Zn (II) removal by alginate - immobilized *Aspergillus fumigatus*

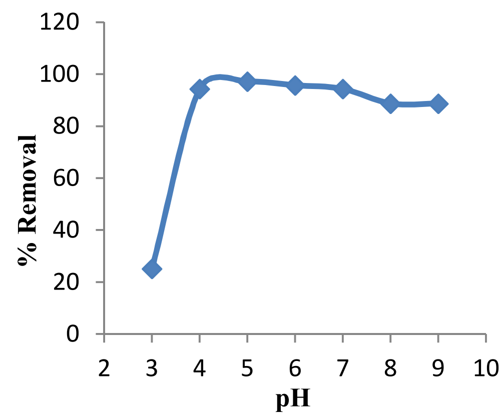

Fig 2 Effect of solution pH on the removal of Zn(II) by alginate immobilized *Aspergillus fumigatus*

The effect of the pH on the removal of Zn (II) ions from solution is presented in Fig 2. The removal percentage increased from 25.14% at pH 3.0 to 97.17% at pH 5.0 after which there was a decrease. At lower pH, heavy metal biosorption decreases due to the positive charge density on metal binding sites i.e. hydrogen ions compete effectively with metal ions in binding to the sites. And with increasing pH, the negative charge density on the adsorbent surface increases due to deprotonation of the metal binding sites. The metal ions then compete more effectively for available binding sites, which increases biosorption (Kapoor and Viraraghvan, 1997).

The effect of the contact time on the removal of Zn (II) ions from solution is presented in Fig 3. From the figure it can be seen that the removal percentage of the Zn (II) ions by *Aspergillus fumigatus* was highest at 10 minutes contact time followed by a marginal decrease afterwards. When an optimum amount had been sorbed, the rate of adsorption decreased and desorption came into play which considerably reduced the overall rate of reaction. The adsorbed ions either blocked access to initial pores or caused particles to aggregate, thereby reducing the active site availability (Garg *et al*., 2004).

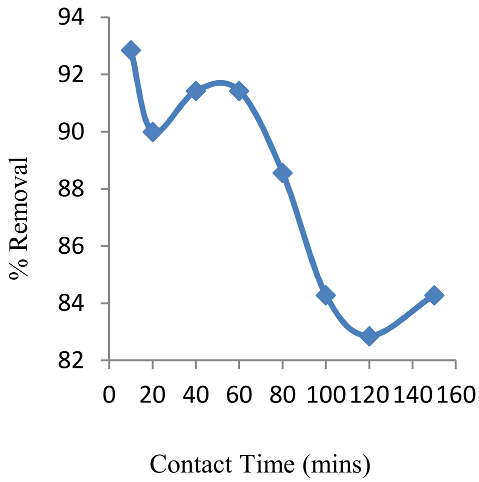

Fig 3 Effect of contact time on the removal of Zn (II) by alginate immobilized *Aspergillus fumigatus*

The effect of initial metal ion concentration on the removal of Zn (II) ions from solution is shown in the Fig 4. From the figure it can be seen that the removal percentage of Zn (II) ions by *Aspergillus fumigatus* increased from 70.11% at 1mg/L to 79.90% at 6 mg/L after which it began to decrease. At lower concentrations, Zn ions in the solution would interact with the binding sites and thus facilitated high adsorption efficiency. At higher concentrations, more Zn ions are left un-adsorbed in solution due to the saturation of binding sites. This indicates that energetically less favourable sites become involved with increasing ion concentrations in the aqueous solution (Arias and Sen, 2009). Similar results have been reported by Amuda *et al*. (2007). The Langmuir isotherm for the biosorption of Zn (II) by alginate – immobilized *A. fumigatus* is shown in Fig 5. The value of the coefficient of determination, R^2, was found to be 0.9072. The R^2 value is close to unity. It, therefore, exhibits a good fit of the equilibrium data for the Langmuir model. Maximum biosorption capacity Q^o was calculated to be 3.55 mg g^{-1}.

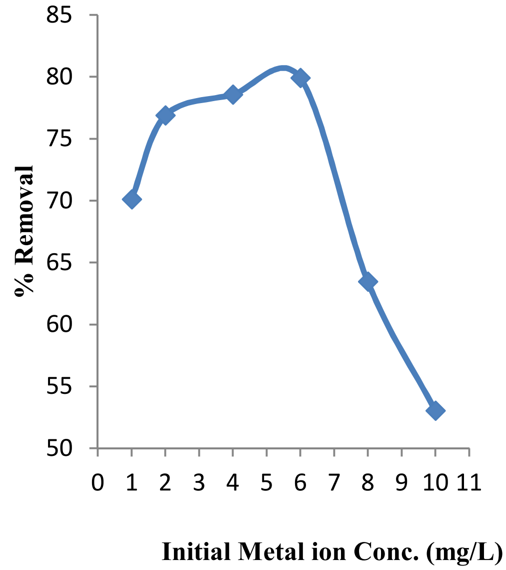

Fig 4 Effects of initial metal ion concentration on Zn (II) removal by alginate immobilized *Aspergillus fumigatus*

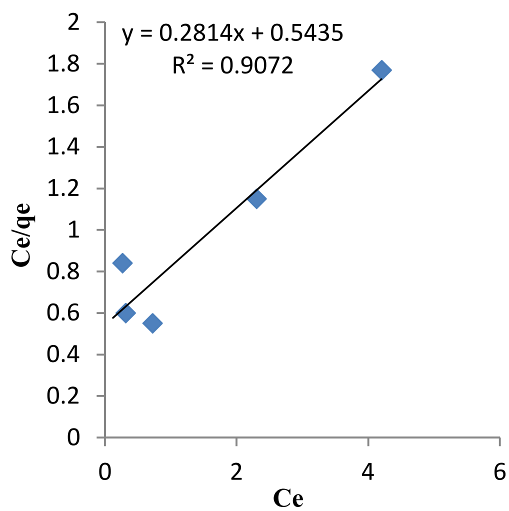

Fig 5 Langmuir isotherm for the biosorption of Zn (II) by alginate immobilized *Aspergillus fumigatus*

*Conclusion***:** The results of the batch adsorption processes undertaken in this study showed that the removal efficiency of the metals was mostly pH – dependent. There was also an increase in efficiency with increase in adsorbent dosage. The adsorption isotherms plotted for the results showed that the experimental data fitted the Langmuir isotherm which indicates a monolayer adsorption. These results indicate that zinc metal removal by biomass of *Penicillium sp* immobilized in alginate is a low cost wastewater treatment option and can be effectively used in small scale treatment plants.

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