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Short Communication

Biosorption of zinc (II) by *Rhizopus arrhizus*: equilibrium and kinetic modelling

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The adsorption of zinc (II) ions on *Rhizopus arrhizus*, a filamentous fungus, was investigated in a batch reactor. Batch adsorption studies were carried out by varying biomass loading. A contact time of 120 min was required to reach equilibrium. Specific zinc (II) uptake decreased with increase in biomass loading and these results were analyzed in light of the Lagergren equation and the process followed a second order rate kinetics. The equilibrium data were analyzed using the Langmuir, Freundlich, Redlich- Peterson and BET adsorption isotherms. The characteristic parameters for each isotherm were determined. All the isotherms provided the best correlation for zinc (II) onto the *R. arrhizus*.

Key words: Zinc, biosorption, *Rhizopus arrhizus*, kinetic models, adsorption isotherms.

INTRODUCTION

"Biosorption" is defined as a process in which solids of natural origin, such as microorganisms (alive or dead) or their derivatives are employed for sequestration of heavy metals from an aqueous environment. The transfer of metal ions from aqueous to solid biosorbent phase can be due to passive, facilitated or active transport. The mechanism of uptake can be due to physical sorption, chemical complexation with microbial cell surface groups or bioaccumulation (Muraleedharan et al., 1991). The presence of considerable amounts of heavy metals in industrial wastewaters poses serious threat to the environmental because the recoveries of heavy metals using conventional chemical methods are not economical (Veglio et al., 1997). The conventional chemical methods include precipitation, ion exchange, electrochemical processes and membrane technology. But all the chemical methods have proved to be much costlier and less efficient than the biosorption process. In addition, chemical methods increase the pollution load on the environment. Biosorption, a biological method of environmental control, can be an alternative to conventional waste-treatment facilities. Biomaterials like fungi have been proven more efficient and economical for removal of toxic metals from dilute aqueous solutions by biosorption because of its filamentous morphology and high percentage of cell walls (Addour et al., 1999). Moreover large quantity of fungal biomass is available from the antibiotic and food industries. Ultimately the biosorption results not only in metal removal but provides an eco-friendly environment.

The performance of biosorption of heavy metal have been predicted using equilibrium isotherms namely; Langmuir and Freundlich, Redlich and Peterson isotherm and BET (Brunauer Emmett Teller) (Zumriye Aksu et al., 1997) and the kinetic models namely, first- order and second- order equations(Zumriye Aksu, 2001). In this work, we studied the sorption of zinc (II) ions from aqueous solutions by *Rhizopus arrhizus*. The kinetics and sorption isotherms of these processes were characterized, and the influence of biomass loading was investigated.

MATERIALS AND METHODS

Chemicals

Reagents were prepared from AR grade chemicals in deionized water obtained from s.d. Fine chem. Ltd., India. A test solution containing zinc (II) was prepared by diluting 1 ml of stock solution of

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metal to the desired concentrations. The ranges of concentrations of zinc (II) prepared from stock solutions varied between 40 and 100 mg/l. A stock solution of aqueous solution of zinc (II) was obtained by dissolving the exact quantity of zinc sulfate in double-distilled water.

Microorganism and growth conditions

Pure culture of *R. arrhizus*, a filamentous fungal cell, was obtained from Institute of Microbial Technology, Chandigarh, India and was immediately transferred to sterile fungal slants of Potato Dextrose Agar media (PDA). Fungal cells were cultivated at 25°C, for a minimum of two days to ensure vigorous growth. The fungal biomass slants were transferred to 50 ml of appropriate sterile growth liquid media containing potato and dextrose. The pH of the media was adjusted to 5.6. The cell suspension was then separated, centrifuged, dried, homogenized and stored for subsequent use.

Immobilization of fungal cells

Calcium alginate beads were produced using 8 g of sodium alginate in 100 ml distilled water and constantly stirring the mixture until the alginate was dissolved. The suspension was dripped into a calcium chloride (2%, w/v) solution. The alginate beads were stored in calcium chloride solution for about 30 min before being rinsed in distilled water twice. Biomass-loaded alginate beads were prepared by mixing 5 g biomass with sodium alginate before extrusion.

Batch biosorption studies

Batch experiments were carried out in Erlenmeyer flasks by adding known weight of immobilized biomass beads in 400 ml of zinc (II) synthetic solutions. The flasks were gently agitated at room temperature on a shaker at 150 rpm constant shaking rate for 2 h to ensure equilibrium. Samples were taken from the solution at predetermined time intervals for the residual zinc (II) ion concentration in the solution. The effect of biomass loading on metal uptake was carried out in the weight range of 2 to 10 g for 100 mg/l zinc (II) concentration at natural pH 6.5 as described above. For the determination of adsorption isotherms, 5 g of biosorbent was suspended in 500 ml solutions containing zinc (II) concentrations in the range of 40 to 100 mg/l at pH 6.5. At the end of predetermined time intervals, the metal concentration in the resulting supernatant was determined.

Analysis of zinc (II) Ions

The concentration of unadsorbed zinc (II) ions in the biosorption medium was determined spectrophotometrically at 620 nm using Zincon as the complexing agent (APHA, 1994).

RESULTS AND DISCUSSION

Biosorption of heavy metal ions using microorganisms are affected by several factors like the initial metal concentration and biomass loading etc. The linearized isotherm plots are given in Figures 1, 2, 3 and 4. The higher correlation coefficients evaluated from the isotherms (>0.98) showed that all the models are very suitable for describing the biosorption equilibrium. In most

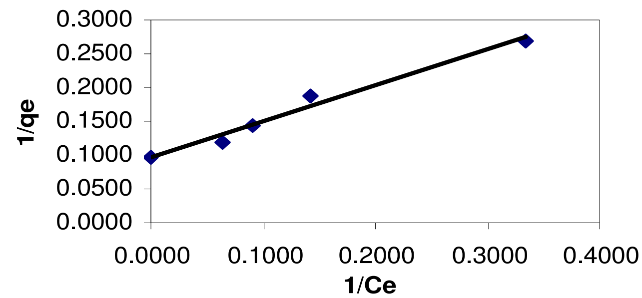

Figure 1. Langmuir plot for the adsorption of zinc (II) by *R. arrhizus*.

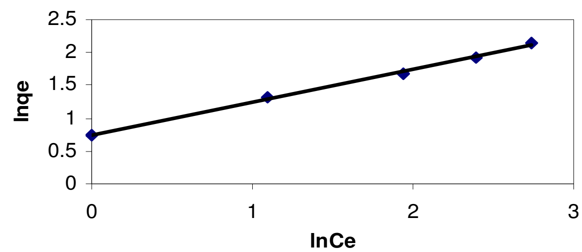

Figure 2. Freundlich plot for the adsorption of zinc (II) by *R. arrhizus*.

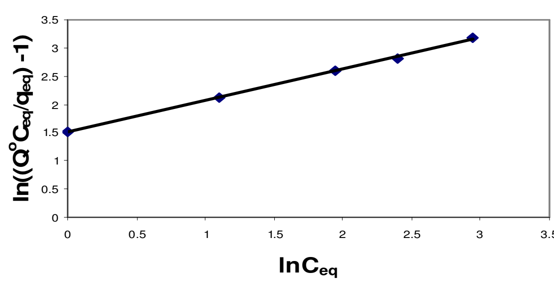

Figure 3. Linearized Redlich-Peterson adsorption isotherm for zinc (II) by *R. arrhizus*.

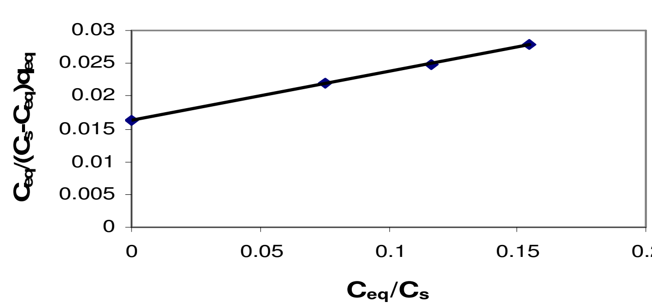

Figure 4. The BET plot for the adsorption of zinc (II) by *R. arrhizus*.

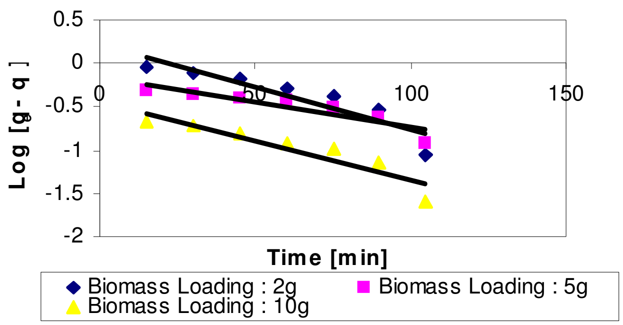

Figure 5. Lagergren plot for zinc (II) removal by *R. arrhizus*.

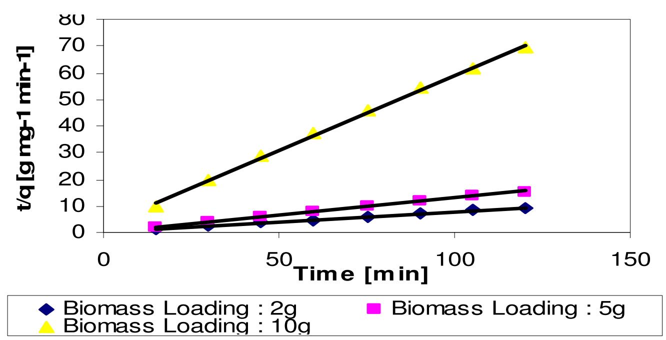

Figure 6. Plots of t/q against contact time for varying biosorbent doses.

cases, the values on n greater than one shows good adsorption (Treybal, 1988). Figure 5 indicates the plots of log (q_{eq}-q) against contact time for varying biosorbent doses. The first order rate constant ($k_{1,ad}$) and q_{eq} values were determined from the slopes and intercepts of Figure 5.

Figure 6 indicates the plots of t/q against contact time for varying biosorbent doses. The second order rate constant ($k_{2,ad}$) and q_{eq} values were determined from the slopes and intercepts of Figure 6. With increase in biomass loading, the specific zinc (II) uptake decreases. This indicates that the increasing biomass concentrations led to insufficiency of metal ions in solution with respect to available binding sites. The results also indicated that the second order rate constants increased with increase in biomass loading. The correlation coefficients for the first order kinetic model obtained at various biomass loading are lower than the second order rate equation; also the calculated q_{eq} values found from the kinetic model was not found to be in good agreement with experimental values.

Figure 5 clearly shows the lack of fit the data for this model as indicated by a large scatter of the experimental points from the line of best fit. A high degree of correlation coefficient was obtained for the second order kinetic model. The theoretical q_{eq} values were found to be in good agreement with the experimental q_{eq} values in this second order kinetics. The results suggest that the sorption system follows the second order kinetics which indicates that the rate controlling step is the chemisorption.

The present investigations showed the different aspects of the biosorption of Zinc (II) by *R. arrhizus*. Results showed that the specific zinc (II) uptake was found to decrease with increase in biomass loading. Linearity observed in the Lagergren plots suggested the second order nature of biosorption. The equilibrium data fitted very well with Langmuir, Freundlich, Redlich-Peterson and BET adsorption isotherms.

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