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Full Length Research Article

BIOSORPTION OF ZINC FROM AQUEOUS SOLUTION BY *PENICILLIUM SP* IMMOBILISED IN CALCIUM ALGINATE

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ABSTRACT

The biosorption of Zn (II) in aqueous solution by alginate-immobilised *Penicillium sp* was investigated. Parameters which are responsible for optimizing sorption such as: initial pH of the solution, contact time and initial Zn (II) concentrations were varied and observed. The results were fitted into Langmuir, Freundlich and Temkin Isotherms. Optimization parameters were focused on initial solution pH, contact time and initial Zn (II) concentrations. Results were fitted to Langmuir, Freundlich and Temkin isotherms. The maximum Zn (II) biosorption of 94.29 % in aqueous solution was achieved at pH of 6.0, contact time of 120 minutes and initial Zn (II) concentration of 1 mg/L. The experimental results showed the R^2 values for the isotherms to be 0.7591, 0.7780 and 0.9552 respectively for the Langmuir, Freundlich and Temkin isotherms indicating that the results fitted the Temkin isotherm more than the other isotherms. The maximum biosorption capacity was 3.78 mgg^{-1} while the value of *n*, a measure of biosorption intensity, was 1.43 Lmg^{-1} showing a favorable adsorption. These results show that immobilized *Penicillium sp* is a good biosorbent for the removal of Zn (II) from waste water with minimal environmental impact.

Keywords: Biosorption, *Penicillium*, Alginate, Isotherm, Adsorption

INTRODUCTION

Heavy metals are very important contaminants of surface and underground water sources. They are often effluents from industries such as metal treatment, mining, fertilizer production or pulp and paper production and enter water systems through untreated waste (Zvinowanda *et al,* 2010). They are elements with high stability and ability to bioaccumulate in the food chain. These metals are extremely toxic even at low concentrations. Thus heavy metal treatment of waste is important in preventing these elements from entering our food chains (Hussain *et al,* 2009). There are several methods for removing heavy metals from wastewater. Some of these methods include chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon etc. (Mathieckal and Yu, 1999). However these methods are expensive and may produce harmful by-products (Zvinowanda *et al,* 2010). The search for new cost-effective technologies for the removal of heavy metal from wastewaters has therefore been directed towards biosorption which involves the use of either live or dead microorganisms or their derivatives.

Biosorption treatment technology has received much attention as it offers low-cost biosorbent and non-hazardous waste product. Previous studies have shown that some microorganisms such as bacteria, algae, yeast and fungi are capable of adsorbing a large amount of metal ions (Ahalya *et al,* 2003). Fungi may be more suitable for the removal of metal from waste water than other microbes because of their great tolerance towards heavy metals and adverse conditions such as low pH (Fourest *et al*, 1994). This study is therefore aimed at examining the sorption capability of alginate – immobilised *Penicillium sp* in the removal of Zn (II) ions from aqueous solution and to verify the environmental factors influencing the biosorption.

MATERIALS AND METHODS

Preparation of Stock Solution

1000 ppm solution Zn (II) metal solution was prepared by dissolving 2.092 g of $ZnC1_2$ in a small volume of distilled water in a beaker and the homogenous solution was poured into a 1 dm^3 volumetric flask and was made up to the mark 1dm^3 with more water. Lower working concentrations were prepared daily from the stock solution by appropriate dilution.

Generation of Biomass

The fungal mycelium of *Penicillium sp* was obtained from Department of Crop Protection, Ahmadu Bello University, Zaria. It was cultured over Potato Dextrose Agar (PDA) plates. The PDA plates of the stock culture were maintained by monthly 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).

Immobilization of Biomass

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.

Adsorption Experiments

The adsorption experiments were carried out by varying one parameter at a time while keeping the others constant. The parameters investigated were effects of solution initial pH, effects of initial metal ion concentration and effects of contact time. The effects of the initial solution pH was investigated by varying the pH of the solution of the ions from 3.0 to 9.0 while keeping the other parameters constant (i.e. initial metal ion concentration, 1 mg/L; solution volume, 50 ml; contact time, 120 minutes; biomass weight, 100 mg and temperature, 29 ^oC). The effects of initial metal ion concentration was investigated by varying the concentration from 1 mg/L to 10 mg/L while keeping the other parameters constant at pH, 5.0; contact time of 120 minutes; solution volume, 50 ml; biomass weight of 100 mg and temperature of 29 ^oC. The effects of contact time on the removal efficiencies were investigated by varying the contact time from 10 to 150 minutes while keeping the other parameters constant (pH, 5.0; metal ion concentration, 1 mg/L; solution volume, 50 ml; biomass weight, 100 mg and temperature, 29 ^oC). The sample vessels 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:

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

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):

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

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.

Langmuir Adsorption Isotherm

This 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.

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

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 (Horshfall *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.

Freundlich Adsorption Isotherm

The Freundlich isotherm was also used to correlate the adsorption equilibrium data in this work. The linearized form of the Freundlich equation is

$$log q_e = log K_f + \frac{1}{n} log C_e \quad \text{.............................} \quad (4)$$

Where q_e (mg/g) is the adsorption density, C_e is the concentration of metal ion in solution at equilibrium (mg/L), K_f and n are the Freundlich constants which determine the curvature and steepness of the isotherm (Akgerman and Zardkorhi, 1996). Also the value of 1/n indicates the affinity of the adsorbate towards the biomass. A plot of 1og Ce against 1og qe gave the value of 1/n and 1og K_f from the slope and the intercept respectively.

Temkin Adsorption Isotherm

The Temkin isotherm model is another isotherm used to study the adsorption process. The Temkin isotherm in its simplified form is given as

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

where $\frac{RT}{b_T}$ = B, q_e is the amount adsorbed at equilibrium and C_e is the residual equilibrium concentration, T is the absolute temperature (K) and R is the gas constant (8.314 J $Mol^{-1}K^{-1}$). The experimental data was fitted into the equation above by plotting q_e against ln C_e and the constants A_T (L/g) and b_T were determined from the slope and the intercept of the plots respectively.

RESULTS AND DISCUSSION

Effect of pH

The effect of the pH on the removal of Zn (II) ions from solution is presented in Fig. 1. The removal percentage increased from 21.23% at pH 3.0 to 94.29% at pH 6.0. This trend can be explained as follows. The pH of the biosorption medium affects the solubility of metal ions and the ionization state of the functional groups. Because of high proton concentration 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).

Effect of initial metal ion concentration

The effect of initial metal ion concentration the removal efficiency is presented in Fig. 2. The removal percentage increased from 11.11% at 1 mg/L concentration to 89.07% at 6 mg/L after which it began to decrease. As can be seen here the percentage removal of zinc increased up to a point then began to decrease. At lower concentrations, Zn (II) ions in the solution would interact with the binding sites and thus facilitated high adsorption efficiency. At higher concentrations, more Zn (II) 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).

Effect of contact time

The effect of the contact time on the removal of Zn (II) ions from solution is presented in Fig. 3. The removal percentage increased from 80.50% at 10 minutes contact time to 89.83% at 40 minutes after which there was a progressive decrease. Equilibrium was therefore attained at 40 minutes. Before attainment of equilibrium the increase in metal sorption could be due to increased electrostatic attraction between the two. 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).

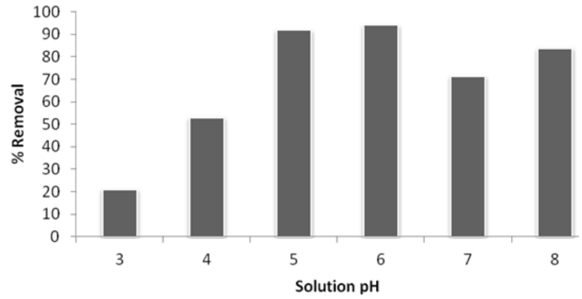

Fig. 1: Effect of pH on the biosorption of Zn (II) ions by alginate – immobilized
Penicillium sp

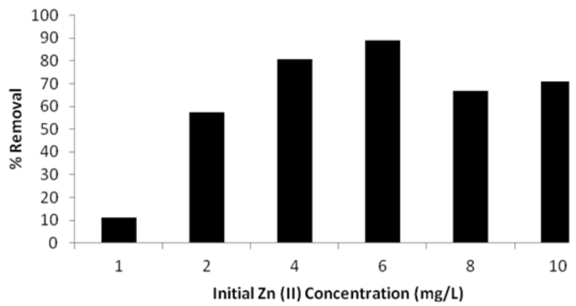

Fig. 2: Effect of initial metal ion concentration on Zn (II) removal by alginate – immobilized
Penicillium sp

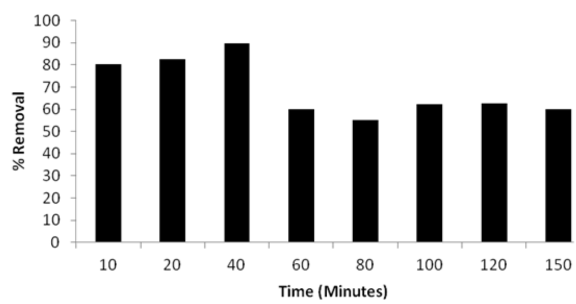

Fig. 3: Effect of contact time on the biosorption of Zn (II) ions by alginate – immobilized
Penicillium sp

Adsorption Isotherms

The Langmuir isotherm for the biosorption of Zn (II) by the alginate – immobilised *Penicillium sp* is shown in Fig. 4. The value of the coefficient of determination, R^2, for the Langmuir equation was found to be 0.7591 while the maximum biosorption capacity Q^o (mg g^{-1}) was calculated to be 3.78 mg g^{-1}. This shows that the adsorption process was not a monolayer adsorption. The Freundlich isotherm plot for the *Penicillium sp* is presented in Fig. 5. The value of the determination coefficient, R^2, for the biosorption of Zn (II) onto *Penicillium sp* was found to be 0.7780 which shows that the biosorption of Zn (II) ions onto the biosorbent has followed the Freundlich isotherm model. The values of K_f and *n* were calculated from slope and intercept of the Freundlich plot between qe and In Ce and they are 1.90 mgg^{-1} and1.43 Lmg^{-1} respectively. The value of *n* lies between 1 and 10 and according to Treybal (1980) this indicates a beneficial adsorption. The Temkin Isotherm for the biosorption of Zn (II) by *Penicillium sp* is presented in Fig. 6. The R^2 value was found to be 0.9552 which indicates that the Temkin isotherm fit well the equilibrium data obtained for the biosorption of Zn (II) onto the biosorbent. Temkin isotherm equation contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. It assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions and the adsorption is uniform distribution of maximum binding energy (Kavitha and Namasivayam, 2007). In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic. The Temkin constant b_T is related to the heat of adsorption; A_T is the equilibrium binding constant (L g^{-1}) corresponding to the maximum binding energy (Pearce et al, 2003). A plot of qe versus In Ce enabled the determination of the isotherm constants A_T and b_T. The value of the constants A_T and b_T were 0.45 L g^{-1} and 2.18 $kJmol^{-1}$ respectively.

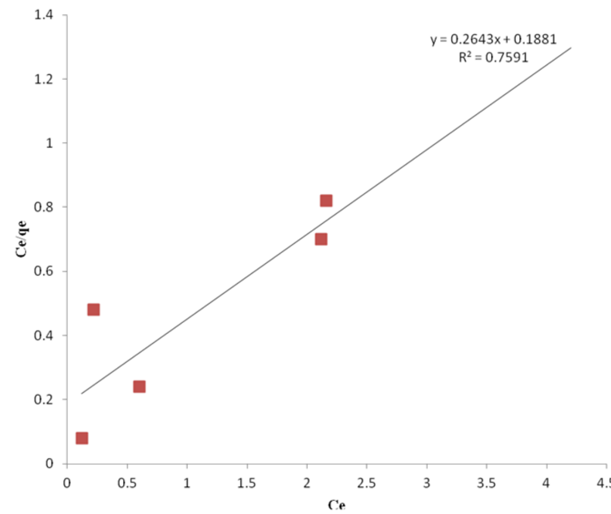

Fig.4. Langmuir isotherm for the biosorption of Zn (II) by alginate – immobilised *Penicillium sp*

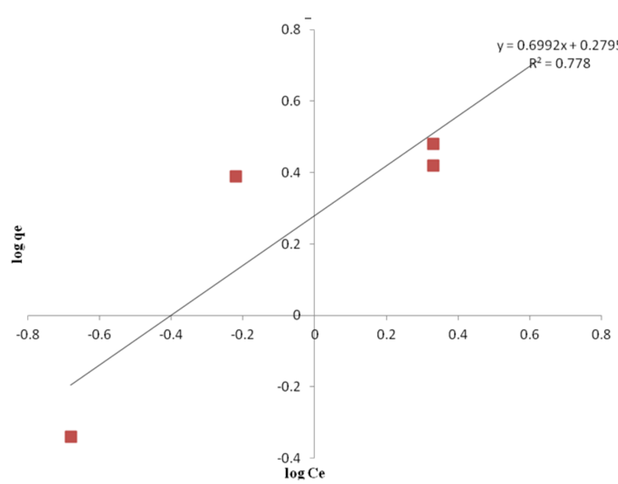

Fig.5. Freundlich isotherm for the biosorption of Zn (II) by alginate – immobilized *Penicillium sp*

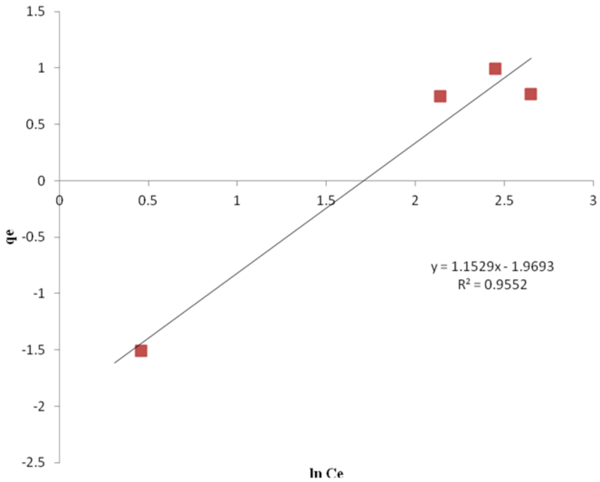

Fig. 6. Temkin isotherm for the biosorption of Zn (II) by alginate – immobilised *Penicillium sp*

Conclusion

The results of the batch adsorption processes undertaken in this study showed that the removal efficiency of the metals was mostly pH – dependent. The results obtained sowed that maximum biosorption was achieved in the range 4.0 – 6.0 (i.e. acidic range). The adsorption isotherms plotted for the results showed that the experimental data did not fit into the Langmuir and Freundlich isotherms well as compared to the Temkin isotherm. However, the Temkin isotherm had a better fit than the Langmuir and Freundlich plots. These results indicate that zinc metal removal by biomass of *Penicillium sp* immobilised in alginate is a low cost wastewater treatment option and can be effectively used in small scale treatment plants.

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