REMOVAL OF ZINC(II) FROM AQUEOUS SOLUTION USING NON-LIVING Oscillatoria sp.

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ABSTRACT

Heavy metal pollution has become one of the major environmental problems in recent years. In this study potential of dried green alga Oscillatoria sp. to remove Zn(II) by biosorption from aqueous solution was evaluated. The algal biomass was found to remove zinc ions efficiently. The rate of biosorption was affected by contact time, pH, initial zinc ion concentration and temperature. Optimal initial pH for Zn(II) sorption was observed to be 6. The uptake of Zn(II) by algal biomass is very rapid in the initial contact time of 10 minutes. Metal uptake capacity of Oscillatoria sp. increased with increase in initial metal ion concentrations. Temperature has been found to have a positive effect on the removal of the zinc by Oscillatoria sp. The experimental data fitted well in both the Freundlich and Langmuir Isotherms ($R^2>0.9828$). $Q_{max}$ obtained from the Langmuir Isotherms was found to be 31.0 mg/g of algal biomass. The sorbed zinc ions were effectively desorbed using 0.1N HCl.

Key Words: Removal, Heavy metals, Biosorption, Zinc, Contact time, pH, Algal biomass, Oscillatoria sp., Temperature, Desorption.

INTRODUCTION

Toxic heavy metals removal from wastewater is essential due to their extreme toxicity towards aquatic life and humans. Public awareness and stringent environmental legislations have led to extensive research into developing effective alternative technologies for the removal of these potentially damaging substances from effluents and industrial wastewaters. Commonly adopted processes for removal of heavy metal ions from wastewater include chemical precipitation, ion exchange and reverse osmosis. These processes are expensive or ineffective, especially when the metal concentrations are very low and of the order of 1 to 100 mg/l in the solution. Biosorption is a promising alternative, which utilizes inactive or dead biomass to bind and concentrate heavy metals from the aqueous solutions. Different types of biomaterials have shown different levels of metal uptake. Among the most promising biomaterials studied is algal biomass.

Zinc is one of the important heavy metals widely used in the electroplating industries. It is an essential element for enzyme activators in humans, but is also toxic at levels of 100-500 mg/day and is a known carcinogen. The present study was aimed at to investigate the removal of Zn(II) from aqueous solutions using non-living Oscillatoria sp. by batch experiments. The
parameters which influence biosorption process such as contact time, pH, initial metal ion concentration, algal dose and temperature were studied. Also desorption of Zn(II) from spent biomass was tested using 0.1N HCl as an eluent.

**MATERIAL AND METHODS**

Algal biomass of *Oscillatoria sp.* was collected from Braham Sarover of Kurukshetra. It was washed under running tap water and was followed by washing with double distilled water to remove extraneous matter. The washed biomass was sun dried and ground to powder in the laboratory pulverizer. The powdered biomass passing through I.S. Sieve No. 30 and retained on I.S. Sieve No. 15 was selected for this study.

Batch forms of kinetic and isotherm sorption experiments were conducted to evaluate effect of contact time, pH, initial zinc ion concentration and temperature. Analytical grade reagents were used in all experiments and double distilled water was used throughout. Stock metal solution (1000 mg/L) was prepared by dissolving 1.000 g of zinc metal (NICE make, Cochin) in minimum volume of (1:1) HCl. It was diluted to one litre with 1 % (V/V) HCl. Zn(II) working solutions were made freshly by diluting the stock solutions. All the experiments, except studies related to the effect of temperature, were conducted at room temperature (28±2°C). Atomic Absorption Spectrophotometer (Model AAS-4129, ECIL, India) was used for metal determinations.

**Procedure adopted for Zn(II) biosorption studies**

100 ml. of zinc metal ion solution of a required concentration (mg/L) was taken in Erlenmeyer flask (250 ml. size). To this solution selected algal dose (g/L) was added and it was put on the rotary shaker (140 rpm). After the desired contact time, the sample was taken out and filtered through Whatman 41 filter paper. The filtrate was analyzed for residual metal ion concentration using Atomic Absorption Spectrophotometer.

**RESULTS AND DISCUSSION**

**Effect of Contact Time**

Fig. 1 shows the effect of contact time on the percentage removal of Zn(II) from aqueous solution with initial Zn(II) concentrations of 10 mg/L by *Oscillatoria sp.* The uptake of Zn(II) by algal biomass is very rapid in the initial contact time of 10 minutes (85-90 % of uptake at equilibrium). It can be observed that maximum percentage removal of Zn(II) was achieved within a period of 100-120 minutes. Therefore, for the following experiments, the contact time was taken as 120 minutes.

![Fig. 1. Effect of contact time on removal of zinc (II) by Oscillatoria sp. at an algal dose of 5, 10, 15 g/L.](image-url)
Effect of initial pH values

Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process\(^4\). Effect of initial pH (pH 1-12) on removal of Zn(II) by Oscillatoria sp. from aqueous solutions is given in Fig. 2. A sharp increase in Zn(II) removal by algal biomass was observed up to pH 4.0 and further it increased slowly being maximum at pH 6.0. Beyond pH 6.0 a slow decline in removal of zinc ions was observed up to pH 10.0, beyond which it reduced sharply. The results indicated that the zinc biosorption by non-living cells of algae was affected by initial pH of the solution and may be due to ionic attraction. Therefore, at low pH values the cell surface becomes more positively charged, reducing the attraction between metal ions and functional groups on the cell walls whereas higher pH helps in metal biosorption, since the metal surface is more charged. Lower biosorption capacity was observed for pH values 6.0-12.0, which may be due to the precipitation and lower polarity of zinc ions at higher pH values.

![Fig. 2. Effect of initial pH on removal of zinc (II).](image)

Effect of algal dose and Initial Metal Ion Concentration

Effect of algal dose was investigated in the initial metal ion concentrations range of 10-100 mg/L and is shown in Fig. 3. It can be observed that percentage removal of Zn(II) increases with increase in algal dose, but the amount of Zn(II) uptake per unit of the algal biomass decreases (Fig. 4). The increase in removal of Zn(II) with increasing dose of the sorbent is expected because for a fixed initial solute concentration, increasing sorbent doses provides greater surface area or sorption sites. The decrease in Zn(II) uptake by biosorbent with increase in algal dose may be due to the dilution of the metal ions with added algal biomass. Maximum uptake of Zn(II) by algal biomass was observed as 24.0 mg/l at an algal dose of 1g/L from the solution with initial metal ion concentration as 100 mg/L.
Effect of Temperature

Effect of temperature on biosorption of Zn(II) by Oscillatoria sp. was studied at three temperatures (20°C, 28°C and 40°C). Initial metal ion concentration, pH and algal dose were kept as 10 mg/l, 6.0 and 2.0 g/L respectively. It can be seen that high temperature enhanced the zinc(II) biosorption by algal biomass (Fig. 5). Temperature affects a number of factors that are important for metal biosorption. These include the stability of the metal ion species; the ligands and ligand metal complex as well as the solubility of the metal ions. In general higher temperature favors greater solubility of metal ions in solution and hence weakens the biosorption of the metals ions\(^5\). Thermodynamically, biosorption will be favored by high temperature if the binding is endothermic but weakened if it is exothermic. The favoring or not by high temperature for the biosorption process is, therefore, dependent on the relative contribution of the carboxylate or amine-ligands on the cell wall/surface. The overall effect of temperature would therefore be the total sum of these favoring and unfavoring factors.
Adsorption Isotherms

Analysis of the obtained equilibrium biosorption data is essential to develop an equation which precisely represents the results and can be used for design purposes. Two widely accepted adsorption isotherm models, linearized Freundlich (Eq.1) and Langmuir (Eq.2) models were tested in the present study.

\[
\log \left( \frac{X}{M} \right) = \log K_f + \left( \frac{1}{n} \right) \log C_e \quad \text{(Eq. 1)}
\]

where \( \frac{X}{M} \) is the amount of metal sorbed per unit dry weight of sorbent (mg/g), \( C_e \) is the concentration of metal in the solution at equilibrium (mg/L), \( K_f \) and \( n \) are the Freundlich constants representing sorption capacity and sorption intensity respectively.

\[
\frac{C_e}{q_{eq}} = \frac{1}{Q_{max} b} + \frac{1}{Q_{max} C_e} \quad \text{.. (Eq. 2)}
\]

The experimental data obtained fitted well \((R^2>0.9828)\) in both the Freundlich and Langmuir Isotherms (Fig. 6 and Fig. 7). The applicability of both the isotherm models implies that both monolayer biosorption and heterogeneous surface conditions exist under the experimental conditions used. The biosorption of Zn(II) on algal biomass is thus complex involving more than one mechanism. \( Q_{max} \) (Maximum possible amount of metallic ions uptake per unit weight of biosorbent, mg/g) obtained from the Langmuir Isotherms was found to be 31.0 mg/g.
CONCLUSION

Recovery of the metal ions sorbed on to the biomass is one of the important aspects of any successful biosorption process development. The studies on the effect of pH on biosorption of zinc (II) showed that binding of the metal is favored at higher pH. This suggests that metal binding at high pH might be reversed at lower pH. Therefore, in the present study, 0.1 N HCl was used to desorb metal ions. The recovery of Zn(II) sorbed on algal biomass was observed to be 93.2%.

REFERENCES

