Removal of Zn(II) from Aqueous Solution by Biosorption using two Green Algal Species *Oscillatoria sp.* & *Spirogyra sp.*

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ABSTRACT

Removal of Zn(II) from aqueous solutions by biosorption on dried green algae *Oscillatoria sp.* and *Spirogyra sp.* was investigated as a function of contact time, pH, algal dose, initial zinc ion concentration and temperature. The uptake of Zn(II) by *Oscillatoria sp.* is rapid than by *Spirogyra sp.* of algae. Metal uptake capacity of algal biomass increased with increase in initial metal ion concentration. *Oscillatoria sp.* was observed to be a superior biosorbent than *Spirogyra sp.* in the removal of zinc ions. Maximum uptake of Zn(II) was observed as 24.2 mg/g and 22.2 mg/g of *Oscillatoria sp.* & *Spirogyra sp.* respectively. Removal of the metal ions has been found to increase with an increase in temperature by both the biomasses. The sorbed zinc ions were effectively desorbed using 0.1N HCl.

Key-Words: Biosorption, algal biomass, contact time, metal uptake, desorption.

1 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 [1]. Major anthropogenic sources of heavy metals include metal extraction, metal fabrication, metal finishing, electroplating, painting, dyeing, surface treatment industry and printed circuit board manufacture. Conventional heavy metal removal processes from aqueous streams include chemical precipitation, ion exchange, filtration, electrochemical treatment, membrane technologies and evaporation recovery. 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 [2]. 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 [3].

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 [4]. The present study was aimed at to investigate the removal of Zn(II) from aqueous solutions using two non-living algal species *Oscillatoria sp.* and *Spirogyra 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. Desorption of Zn(II) from spent algal biomasses was tested using 0.1N HCl as an eluent.

2 MATERIALS AND METHODS

Algal biomass of *Oscillatoria sp.* was collected from Braham Sarover and *Spirogyra sp.* was collected from Sannihit Sarover of Kurukshetra. These biomasses were washed under running tap water which was followed by washing with double distilled water to remove extraneous matter. The washed biomasses were sun dried and ground to powder in the laboratory pulverizer. The powdered biomass passing through I.S. Sieve No. 30 (aperture size 300 micron) and retained on I.S. Sieve No. 15 (aperture size 150 microns) was selected for this study.

Batch forms of kinetic and isotherm sorption experiments were conducted to evaluate effect of contact time, pH, initial nickel 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^oC). 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.

3 RESULTS AND DISCUSSIONS

3.1 Effect of Contact Time

Fig. 1 shows the effect of contact time on the percentage removal of Zn(II) from aqueous solutions with initial Zn(II) concentrations of 10 mg/L by algal biomasses at an algal dose of 5 g/L. Algal biomass of *Oscillatoria sp.* was observed to be a faster biosorbent than *Spirogyra sp.* for removal of zinc(II). The percentage removal of Zn(II) by *Oscillatoria sp.* was more than 94 % of final removal at equilibrium time within first 20 minutes where as it was around 76 % by *Spirogyra sp.* of algae. Although the rate of percentage removal in the beginning (say at 10, 20 minutes of contact time) was different by both algal species but as the contact time increased the difference in percentage removal went on reducing. It can be seen that maximum percentage removal of Zn(II) was achieved within a period of 120 minutes. Therefore, for the following experiments, the contact time was taken as 120 minutes.

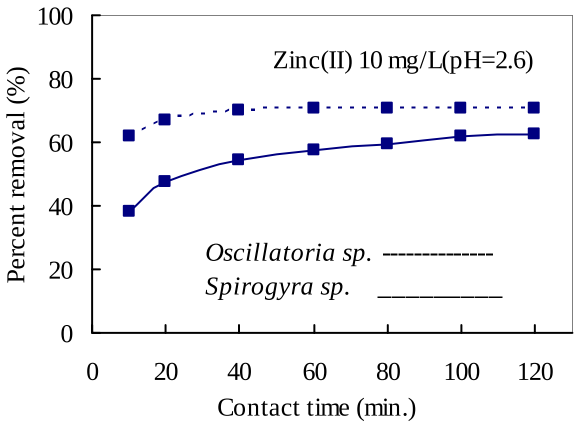

Fig. 1 Effect of contact time on removal of zinc(II) at algal dose 5 g/L.

3.2 Effect of Initial pH Values

The pH of the aqueous solution is an important parameter affecting the biosorption process [5, 6]. Effect of initial pH (pH 1-12) on removal of Zn(II) by biomasses from aqueous solutions is given in Fig. 2. A general increase in zinc(II) biosorption up to pH 4.0 by both algal species was observed and with increase in pH value to 6.0, there was not much change in zinc(II) removal. Removal of zinc(II) by *Oscillatoria sp.* & *Spirogyra sp.* was observed to be maximum at pH 6.0 and it decreased slowly further. Zinc will transform into hydroxide complex at higher pH and could not be considered for biosorption behavior of the cells [7]. The results indicated that the zinc biosorption by non-living cells of algal biomasses 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.

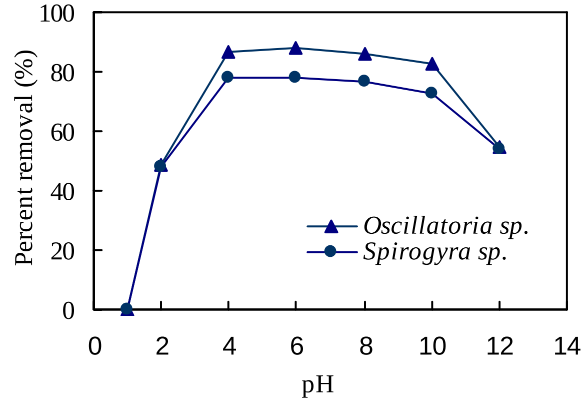

Fig. 2. Effect of initial pH on removal of zinc(II) algal dose 5 g/L and initial Zn(II) conc. 10 mg/L.

3.3 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 & 4. It can be observed that percentage

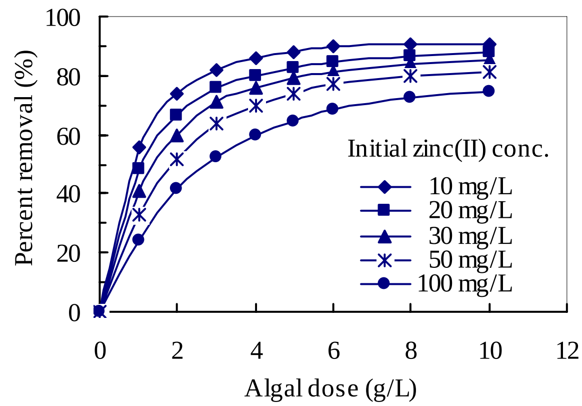

Fig. 3 Effect of algal dose (*Oscillatoria sp .*) on zinc(II) removal at initial pH 6.0.

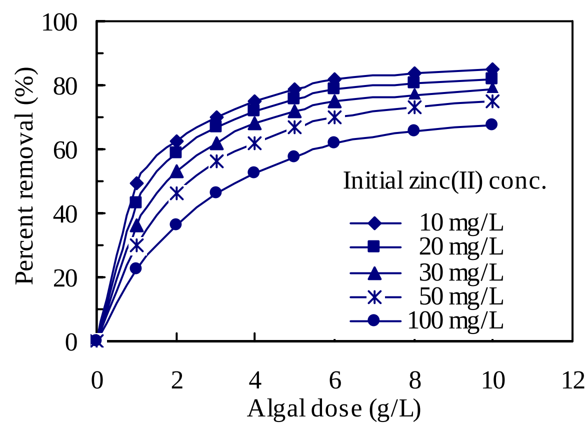

Fig. 4 Effect of algal dose (*Spirogyra sp.*) on zinc(II) removal at initial pH 6.0.

removal of Zn(II) increases with increase in algal dose. The increases 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. It is evident that *Oscillatoria sp.* invariably maintained an upper hand in respect of metal removal over *Spirogyra sp.* at all the algal doses. With an algal dose of 10 g/L, the removal of Zn(II) was observed as 90.9% by *Oscillatoria sp.* whereas it was 84.8% by *Spirogyra sp.* from aqueous solution of Zn(II) conc. of 10 mg/L. The differences between algal species in the metal ion binding capacity may be due to the properties of the algae (structure, functional groups and surface area etc.). Cell walls of algae contain polysaccharides as basic building blocks, which have ion exchange properties and also proteins and lipids and therefore offer a host of functional groups capable of binding to heavy metals. These functional groups such as amino, carboxylic, sulphydryl, phosphate etc. differ in their affinity and specificity for metal binding [6].

It can be observed that the amount of Zn(II) uptake per unit of the algal biomass decreases with

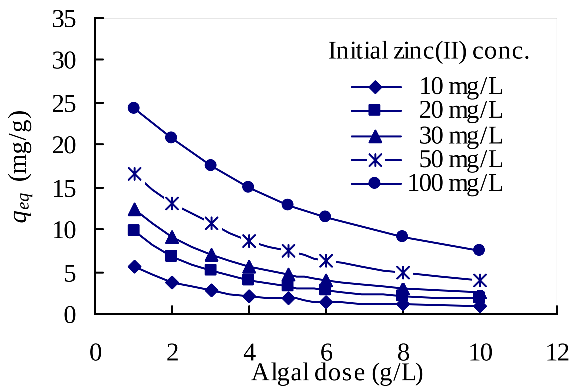

Fig. 5 Effect of algal dose and initial metal ion concentration on specific uptake (q_{eq}) of zinc(II) by *Oscillatoria sp.* at initial pH 6.0.

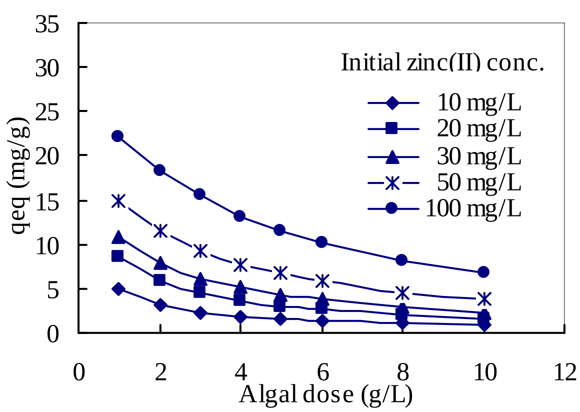

Fig. 6 Effect of algal dose and initial metal ion concentration on specific uptake (qeq) of zinc(II) by Spirogyra sp. at initial pH 6.0.

increase in algal dose (Fig. 5 & 6). 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 biomasses was observed as 24.2 mg/g and 22.2 mg/g of *Oscillatoria sp.* & *Spirogyra sp.* respectively.

3.4 Effect of Temperature

Effect of temperature on biosorption of Zn(II) by algal species was studied in the temperature range of 20-40ºC. Initial Zn(II) 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 Zn(II) biosorption by algal biomass (Fig. 7). The increase in metal ions removal was observed more in the case of *Oscillatoria sp.* than *Spirogyra sp.* The increase in biosorption with temperature indicates an endothermic process. 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 [8]. 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.

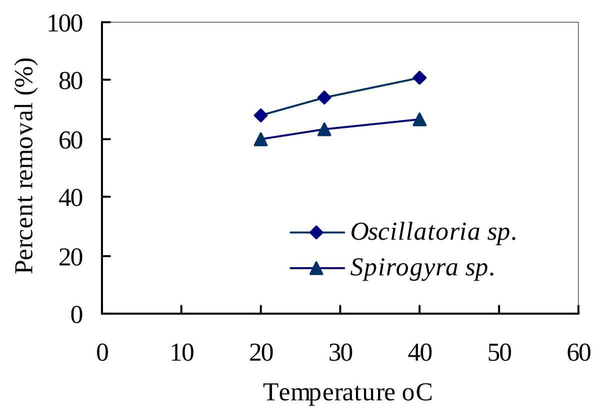

Fig. 7. Effect of temperature on removal of Zn(II) by algal biomass at Zn(II) initial conc. 10 mg/L.

3.5 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.

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$$Log\left(\frac{X}{M}\right) = \log\ K_f\ + \left(\frac{1}{n}\right)\log\ C_e \quad (1)$$

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.

$$\frac{C_e}{q_{eq}} = \frac{1}{Q_{\max}\, b} + \frac{1}{Q_{\max}} C_e \quad (2)$$

where, q_{eq} is the amount of metal sorbed per unit dry weight of sorbent at equilibrium (mg/g), C_e is the residual (equilibrium) metal ion concentration left in solution after binding, Q_{max} is the maximum possible amount of metallic ion sorbed per unit weight of sorbent and b is the equilibrium constant related to the affinity of the binding sites for the metal ions.

The experimental data obtained fitted well (R^2>0.98) in both the Freundlich and Langmuir Isotherms (Fig. 8 & 9). 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 biomasses 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 and 29.7 mg/g for *Oscillatoria sp.* & *Spirogyra sp*. respectively.

3.6 Desorption

Recovery of the metal ions sorbed onto the biomass is one of the important aspects of any successful biosorption process development [9]. The studies on the effect of pH on biosorption of Zn(II) on ***Oscillatoria sp.*** and *Spirogyra sp.* 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. More than 93.2% recovery of Zn(II) sorbed on *Oscillatoria sp* observed where as it was around 89% in the case of *Spirogyra sp*. .

4 CONCLUSIONS

Algal biomasses of ***Oscillatoria sp.*** and *Spirogyra sp.* demonstrated a good capacity of zinc removal by biosorption, highlighting their potential for effluent treatment processes. The removal of Zn(II)by algal biomass is highly dependent on pH. It is also affected by factors such as contact time, initial metal ion concentration and temperature. ***Oscillatoria sp.*** was observed to be a superior biosorbent than *Spirogyra sp.* in the removal of zinc ions. With an algal dose of 10 g/L, the removal of Zn(II) was observed as 90.9% by *Oscillatoria sp.* whereas it was 84.8% by *Spirogyra sp*. from aqueous solution of Zn(II) conc. of 10 mg/L. Q_{max} obtained from the Langmuir Isotherms was found to be 31.0 mg/g and 29.7 mg/g for *Oscillatoria sp.* & *Spirogyra sp*. respectively. Desorption of the sorbed Zn(II) by 0.1N HCl indicated that recovery of Zn(II) from spent biomass is possible. It can be concluded that non-living ***Oscillatoria sp.*** and *Spirogyra sp.* of algae can be considered as an inexpensive, effective and easily available in abundance biosorbent for the removal of Zn(II) from aqueous solutions.

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