BIOSORPTION OF COPPER(II) FROM AQUEOUS SOLUTION BY NON-LIVING *Spirogyra* sp.

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ABSTRACT

The biosorption of Cu(II) by a dried green alga *Spirogyra* sp. was investigated. Optimal initial pH for Cu(II) sorption was found to be 4. The uptake of Cu(II) by algal biomass is very rapid in the initial contact time of 10 minutes. Metal uptake capacity of *Spirogyra* sp. was found to be increasing with increase in initial metal ion concentrations. When the initial Cu(II) concentration was increased from 10 to 100 mg/L, metal uptake of biomass increased from 6.2 to 23.9 mg/g of biomass. The experimental data fitted well in both the Freundlich and Langmuir Isotherms ($R^2$>0.9819). $Q_{max}$ obtained from the Langmuir Isotherms was found to be 28.7 mg/g of biomass.

Key Words: Biosorption, Heavy metals, Biosorbent, Contact time, pH, Metal uptake, Desorption.

INTRODUCTION

Pollution due to heavy metals has become an environmental problem of worldwide concern due to their increased discharge, toxicity, non-biodegradable and persistence nature. Major anthropogenic sources of heavy metals include metal extraction, metal fabrication, metal finishing, electroplating, painting, dyeing, surface treatment industry and printed circuit board manufacture$^{1,2}$. 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$^3$. 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$^4$. Algal surfaces (cell wall/mucilage) have been found containing different functional groups such as carboxyl, hydroxyl, sulphate and other charged groups, which are created by their carbohydrate, protein and lipid components and are believed be responsible for impressive metal uptake$^5$. In the present work the biosorption capacity of non-living *Spirogyra* sp. (fresh water alga) for Cu(II) from aqueous solutions was investigated by batch experiments. The parameters which influence biosorption process such as contact time, pH, initial metal ion concentration and algal dose were studied. Also desorption of Cu(II) from spent biomass was tested using 0.1 NHCl as an eluent.
MATERIAL AND METHODS

Algal biomass of Spirogyra sp. was collected from Sannihit 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.

Analytical grade reagents were used in all experiments and double distilled water was used throughout. Cu(II) working solutions were made freshly by diluting the stock solutions (1000 mg/l). All the experiments were conducted at room temperature (28±2°C). Atomic Absorption Spectrophotometer (Model AAS-4129, ECIL, India) was used for metal determinations.

Procedure adopted for Cu(II) biosorption studies:

100 ml. of copper 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

The effect of contact time on the percentage removal of Cu(II) from synthetic solutions with initial metal ion concentration of 10 mg/l for copper(II) using the algal dose of 5, 10 and 15 g/l are shown in Fig. 1. It can be observed that maximum percentage removal of metal 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 Cu(II) by Spirogyra sp. at algal dose of 5, 10 and 15 g/l](image-url)
Effect of initial pH values

Earlier studies on heavy metal biosorption have shown that pH is one of the most important parameter affecting the biosorption process. The effect of initial pH was observed on biosorption of Cu(II) from solutions at pH 1-8 (Fig. 2) The uptake of copper(II) increased with an increase in pH from 1-4. Beyond pH 4, a progressive decrease in Cu(II) removal was observed. The results indicated that the copper 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. Copper will transform into hydroxide complexes at higher pH and could not be considered for biosorption behaviour of the cells.

![Graph showing effect of initial pH on removal of copper (II)](image)

**Fig. 2.** Effect of initial pH on removal of copper (II)

Effect of algal dose and initial metal ion Concentration

Biosorption experiments were conducted keeping the initial pH values of copper solutions as 4. Effect of algal dose was investigated in the initial metal ion concentrations range of 10-100 mg/l (Fig. 3). It is evident from figure that the lower algal dose (1-4 g/l) was more effective for all the initial concentrations of copper removal. Beyond 4 g/l algal dose, it was slowed down, a further increase in algal dose couldn’t cause any appreciable increase in the rate of metal removal. These results clearly indicate that the removal efficiency increases upto the optimum dosage beyond which the increase in removal efficiency is negligible. It is apparent that the equilibrium metal ion concentration decreases with increasing algal dosage for a given initial metal concentration. This is to be expected because, for a fixed initial solute concentration, increasing sorbent doses provides greater surface area or sorption sites. But after optimal dose sorption sites were not easily accessible and making sorption rate almost constant. Metal uptake, $q_{eq}$ (mg of metal ion uptake per g of alga at equilibrium) by the *Spirogyra sp.* is shown in Fig. 4. It can be seen that the
metal uptake showed a decreasing trend i.e.
high metal uptake at lower algal doses and
lower uptake at higher algal doses. In other
words, though the metal removal is directly
proportional to the increase in algal dose
but metal uptake by algal biomass is
inversely proportional to the increase in algal
dose from the metal solution. This decrease
may be due to the dilution of the metal ions
with added algal biomass. Maximum uptake
of Cu(II) by algal biomass was observed
as 23.9 mg/l at an algal dose of 1 g/l from
the solution with initial metal ion
concentration as 100 mg/l. The increase of
loading capacities of the algal species with
the increase of metal concentration may be
due to higher probability of collusion
between metal ions and biosorbents.

![Graph showing effect of algal dose on copper (II) removal (%) at initial pH 4.0](image1)

**Fig. 3.** Effect of algal dose on copper (II) removal (%) at initial pH 4.0

![Graph showing effect of algal dose and initial metal ion concentration on specific uptake ($q_{eq}$) of copper (II) by Spirogyra Sp. at initial pH 4.0](image2)

**Fig. 4.** Effect of algal dose and initial metal ion concentration on specific uptake ($q_{eq}$) of copper (II) by Spirogyra Sp. at initial pH 4.0
Adsorption Isotherms

Freundlich and Langmuir isotherm models were used to evaluate the biosorption behaviour of *Spirogyra sp*. The experimental data obtained fitted well in both the Freundlich and Langmuir Isotherms ($R^2>0.9819$). 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 Cu(II) on algal biomass is thus complex involving more than one mechanism. $Q_{\text{max}}$ (Maximum possible amount of metallic ions uptake per unit weight of biosorbent, mg/g) obtained from the Langmuir Isotherms was found to be 28.7 mg/g.

Desorption of Metals

Recovery of the Cu(II) sorbed onto the biomass is one of the important aspects of any successful biosorption process development. The studies on the effect of pH on biosorption of copper (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 Cu(II) sorbed was found to be 92.3%.

CONCLUSION

The results showed that *Spirogyra sp*. can be used as an biosorbent for the effective removal and recovery of Cu(II) from aqueous solutions. The biosorption is pH dependent and maximum removal occurs at pH 4. The applicability of both the isotherm models implies that both monolayer biosorption and heterogeneous surface conditions exist under the experimental conditions used. The sorbed Cu(II) can recovered using 0.1 N HCl.

REFERENCES