Biosorption of copper from aqueous solution using algal biomass

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Sorption experiments using the dead biomass of Spirogyra species, for copper removal were carried out to study the influence and optimization of the biosorption of Cu (II). The effect of pH (1.0 - 10.0), initial metal ion concentration (1 - 100ppm), different contact periods (30 - 180 min), varying temperature (25 – 50 ºC) and varying biomass quantities (0.5, 1.0, 1.5 and 2.0 g) were also examined. It was observed that Spirogyra species possessed better specific uptake capacities for Cu (II), showing approximate uptake of 34.94mg/g of biomass. Spirogyra species has shown much better sorption in the pH between 6.0 - 7.0 and at contact time of 30 min.

Keywords: Biosorption, Copper (II), Algal biomass, Spirogyra

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Introduction

A remarkable increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. There has been increasing concern because of their known accumulation in the food chain and persistence in nature1,2. Heavy metals such as, chromium, copper, zinc, and nickel, in wastewater, are hazardous to the environment. Copper finds its way to water bodies through wastewater from Cu wire mills, coal burning industries, electroplating, tanning, smelting and refining, insecticides, fungicides, and iron and steel producing industries.3 According to IS: 2296-1974 the maximum permissible limit of copper in inland surface water used for public water supply and bathing is 1.0mg/L and according to IS: 3306-1974 and IS: 7968-1976, the tolerance limit of Cu for industrial effluent discharged is 3.0mg/L. A viable and safe disposal of Cu sludge has not yet been identified worldover. Some important methods used are ion exchange, reduction and precipitation, evaporative recovery, electrolysis, ion floatation, and reverse osmosis. Many of these methods require high capital and recurring expenditures and consequently are not suitable for industrial use.4 Therefore, an alternate process for the removal of heavy metal ion, using microorganisms has been proposed. Various types of microbial biomass-algae, fungi, bacteria and yeast, can serve as a basis for producing potent metal sequestering biosorbents.5 Because of this property more economical and efficient techniques, based on microbes have been developed for adsorption of heavy metals.

Biosorption is possible by both living and non-living biomass. There are two modes of metal ion uptake. The first mode is independent of cell metabolic activity, and is referred to as biosorption or passive uptake. It involves surface binding of metal ions to cell wall. This mode is common to both living and dead cells. The second mode of metal uptake into the cell across the cell membrane is dependent on the cell metabolism, and is referred to as intracellular uptake, active uptake or bioaccumulation. This mode occurs in living cells only.6 In this study, dead biomass of filamentous algae Spirogyra was used.

Materials and Methods

Spirogyra species, a cheaply available green filamentous algae belonging to the family chlorophyceae was used as sorbent to find its capacity for Cu (II) removed. The effect of various other parameters on the removal efficiency was determined.

Preparation of Biomass

Algal biomass was collected from the mansar lake, Jammu & Kashmir, India, where these are available in abundance. After collecting required amount, it was thoroughly washed with distilled water to remove dirt...
and other unwanted material and water was squeezed out. Biomass was then dried at 50°C overnight and crushed. It was sieved to select particles 300 µm in size for use.

Preparation of Copper Solution

The solutions of copper (II) were prepared by diluting a 100 ppm stock metal ion solution obtained by dissolving 0.393 g of hydrated copper sulphate (CuSO₄.7H₂O) in 1 L distilled water. The range of concentrations of prepared Cu (II) solution was 1-100 ppm. The range of pH selected was 1.0° - 10.0. The pH of each solution was adjusted to the required value with 1N HCl and 1N NaOH before mixing the dead biomass with the solution.

Biosorption Studies

A known quantity of biomass powder was contacted with a known concentration of metal bearing solution (0.5g biomass in 100mL metal ion solution in an Erlenmeyer flask). Samples were taken out at specific duration of time and centrifuged at 5000rpm for 10 min. The supernatant liquid was separated and analyzed for Cu (II) ions.

Analysis of Cu (II) Ions

Perkin Elmer 2380 atomic absorption spectrophotometer was used to determine the concentration of Cu (II) in the solution.

Results and Discussion

The biosorption of heavy metal ions by microorganisms is affected not only by the surface properties of the organisms but also by various other physico chemical parameters of metal ion solution. Therefore the effect of contact time, temperature, and varying amounts of biomass on the removal of Cu (II) ions by the dead algal biomass was investigated.

Metal Removal as a Function of Time

The adsorption data for the uptake of metal ions vs contact time for different algal doses, i.e 0.5, 1.0, 1.5 and 2.0g/L at natural pH are shown in Fig. 1. These plots indicate that equilibrium reaches nearly at about 30 min of contact time. The removal of Cu (II) range between 58 – 85 per cent at 30 min at initial concentration of 20mg/L with various algal doses at natural pH. The rate of Cu (II) binding with algal biomass is more at initial stages, which gradually decreases and remains almost constant after an optimum time. At equilibrium, removal of metal ions attains a constant value, because adsorption and desorption balance each other. Similar results has been reported for biosorption uptake of copper by Pseudomonas aeruginosa. ⁷

Effect of Varying Biomass Concentration

Effect of adsorbent dose has been studied by varying the amount of adsorbents from 0.5-2.0g/L at normal pH. Results show that the maximum removal of Cu (II) is obtained at minimum dose of 0.5g/L, i.e with increase in dose, there was decrease in percentage removal from 85–58 per cent. Copper uptake decreases when biosorbent concentration increases. The higher biomass concentration caused screen effect of dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit biomass. ⁸

Effect of Initial Metal Ion Concentration

The adsorption capacities, determined at different initial Cu (II) ion concentration at adsorbent dose of 0.5g/L and contact time of 30 min at normal pH are compared in Fig. 2. It is evident from the Fig. 2 that as the concentration of Cu (II) increases the percentage removal efficiency increases. In the present study, this increase was observed from 52–91
BISHNOI et al.: BIOSORPTION OF COPPER USING ALGAL BIOMASS

815

per cent during concentration, variation from 1 to 40mg/L but further decreases with increase in concentration similar results were observed by fungal pellets.⁹

Effect of Temperature on Adsorption

The relationship between percentage removal and contact time at different temperatures, i.e 25, 30, 40 and 50°C, respectively at normal pH and optimum algal dose of 0.5g/L is given (Fig. 3). After 30 min, thermal equilibrium was achieved and the percentage removal of Cu (II) decreased from 83–38 per cent with increase in temperature from 25-50°C. At optimum temperature (25°C), percentage removal ranges between 83–87 per cent for different contact time (30-180 min).

Effect of pH on Adsorption

To evaluate the effect of hydrogen ion concentration on the adsorption behavior of Cu (II) on algae, studies were conducted with pH between 1.0-10.0 and the results are shown in Fig. 4. An increase in percent removal with increase in pH of the medium was observed for the metal ion to a pH value of 7.0. There was decrease in percent removal above this pH. It has been indicated that on increasing the pH from 1.0-7.0 of the medium the sorption capacity increased from 31–86 per cent. The results suggest that the absorption of Cu to the biomass is mainly due to ionic attraction. Therefore, as pH decreases the cell surface becomes more positively charged, reducing the attraction between biomass and metal ions. In contrast, higher pH results in facilitation of metal uptake, since the cell surface is more negatively charged. An optimum pH of 6.5 for the adsorption of copper was found using Saccharomyces cerevisiae as the biosorbent.¹⁰

Adsorption Isotherm for Copper

Isotherm data was used to calculate the ultimate sorption capacity of the green algae by substitution, the required equilibrium concentration in the Freundlich equation:

\[ q_e = k_f C_e^{1/n} \]

Table 1 summarizes the Freundlich constants for Cu (II) along with correlation coefficient (\( r^2 \)). High \( r^2 \) values indicate that there is strong positive relationship in the data. A plot between log \( q_e \) and log

<table>
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<th>Initial Cu(II) conc. (mg/L)</th>
<th>( r^2 )</th>
<th>( \log k_f )</th>
<th>( K_f )</th>
<th>( 1/n )</th>
<th>( n )</th>
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</table>

Table 1 — Constant for Freundlich isotherms of Cu(II) for algae

![Fig. 3 — Effect of temperature on percent removal of Cu(II) at different contact time by green algae](image)

![Fig. 4 — Effect of pH on percent removal of Cu(II) by green algae](image)

![Fig. 5 — Linearized Freundlich isotherm for the adsorption of Cu(II) on green algae](image)
$C_e$ yields a straight line. Fig. 5 gives the linearized form of Freundlich isotherm.

**Conclusions**

A study pertaining to the assessment of the best adsorption parameters and quantitative analysis of Cu (11) uptake by *Spirogyra* species was done. Optimization of conditions for biomass adsorption revealed that at pH – 6.5; Cu (11) concentration – 20 mg/L; biomass dose – 0.5 g/L; at -25 °C; and contact time -30 min maximum adsorption occurred. At the above conditions biomass could bind approximately 35 mg Cu/g biomass.

**References**