Biosorption of Copper(II) Ion From Aqueous Solutions Using Caucasian Fir (*Abies nordmanniana* (Stev.) Spach. subsp. *nordmanniana*) Cones

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In the present study the biosorption characteristics of Cu(II) ions from aqueous solution using the cone Caucasian fir biomass were investigated. Optimum biosorption conditions were determined as a function of initial metal ion concentrations, biomass dosage, pH and contact time. Caucasian fir cones exhibited the highest copper(II) uptake capacity at the initial pH value of 5.0 in 1 h, 6 g/L biomass dosage and initial copper(II) ion concentration of 50 mg/L. The removal of copper(II) from aqueous solution increased with pH and sharply decreased when pH of the solution was decreased. At the optimal conditions, copper(II) ion biosorption was decreased as the initial metal concentration increased. Freundlich and Langmuir models were applied to describe the biosorption isotherm of the metal ions by Caucasian fir biomass. Both models were found to exhibit good fits to the experimental data.

Key Words: Biosorption, Copper, Caucasian fir cones, Isotherm.

INTRODUCTION

Heavy metal pollution of aquatic environment has been a great concern in a few decades due to their non-biodegradability and toxicity. These metals are introduced into aquatic system significantly as a result of various industrial processes such as metal finishing, electroplating, mining, metallurgy, tanning, chemical manufacturing and battery manufacturing[1]. One of the most important heavy metals is copper. Copper is one of the heavy metals which are most harmful to living organisms and one of the widespread heavy metal contaminants in our environment. Copper present in industrial wastes is primarily in the form of the bivalent Cu(II) as a hydrolysis product, $CuCO_3$(aq) and/or organic complexes. Several industries, for example, refineries, paper and pulp, fertilizer, copper/brass plating and copper-ammonium rayon, release undesired amounts of Cu(II) ions[2-4]. In the copper-cleaning, plating and metal-processing industries, Cu(II) concentrations approach 100-120 mg/L, respectively. This value is very high in relation to water quality standards and Cu(II) concentrations of wastewaters should be reduced to a value of 1.0-1.5 mg/L[5]. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney[6].

Several methods were proposed for Cu removal from waste waters such as chemical precipitation, phytoextraction, ultrafiltration, chemical oxidation or reduction, evaporation, adsorption and ion exchange[7,8]. However, technical or economic factors restrict sometimes the feasibility of such techniques[9,10]. For example, ion exchange and adsorption processes are very effective but require expensive adsorbent materials. Biosorption as a wastewater treatment process has been found to be an economically feasible alternative for metal removal.

In the last decade Algae[11], fungus[12,13], microorganism[14], sunflower stalks[15], *Eucalyptus bark*[16], *Hevea brasilinesis* sawdust[17], oak sawdust[18], *Tamarindus indica* seeds[19], *Pinus sylvestris* cones[20], yeast[21] or their separated components have been used successfully as biosorbent for heavy metal removal.

Caucasian fir spread naturally in the Caucasus, Georgia, the East Black Sea and the northern parts of Armenia. It occurs at altitudes of 900-2200 m on mountains. Caucasian fir is one of the most important species grown for Christmas trees in the northeast Europe countries[22]. In addition to this, it is also a popular ornamental tree in parks and large gardens. The cones are 10-20 cm long and 4-5 cm broad, with about 150-200 scales and cylindrical and keep on plentiful resin[22]. Cone biomass was a waste itself and a readily available biosorbent[20]. The ovulate cone is the well known cone of the *Abies*, *Pinus*, *Picea* and other conifers.

The objective of the present work is to investigate the biosorption potential of Caucasian fir cones in the removal of Cu(II) ions from aqueous solution. The effects of pH, biomass dosage, contact time and initial metal concentration on the biosorption capacity of cones were studied. The Langmuir and Freundlich models were used to describe equilibrium isotherms.

EXPERIMENTAL

Biosorbent preparation: Caucasian fir cones were used in this investigation. They were washed with deionized water and dried at 80 °C for 24 h. The dried biomass was ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve.

Solution preparation: The metal stock solution of Cu was obtained by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ salts in double distilled water. Calculated quantities of this stock solution were measured and used for further experimental solution preparation.

Batch biosorption studies: The metal solutions were prepared by diluting 1.0 g/L stock solutions. The range of concentrations of prepared Cu solution varied from 5-100 mg/L. Biosorption experiments were carried out in 250 mL Erlenmeyer flasks using 100 mL metal bearing solution with a known quantity of the dried biosorbent. Before mixing with the cone biomass for effect of pH, the pH of each solution was adjusted to desired values with HCl and NaOH. The biosorption medium was placed in a mechanical platform shaker (Thermolyne ROSI 1000) and stirred for 1 h at 25 °C at a fixed agitation speed of 200 rpm. The samples were taken at definite time and

were filtered immediately to remove biomass by filter paper (Whatmann GF/A) and Cu(II) in the remaining solution were analyzed. The Cu(II) biosorption equilibrium was modeled by using the Freundlich and Langmuir models at the optimum pH value of solution.

Analysis of Cu(II) ions: The concentration of unadsorbed Cu ions in the effluent was determined using an atomic absorption spectrophotometer (Perkin-Elmer Analyst 360).

RESULTS AND DISCUSSION

Effect of pH: pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions[23]. pH affects not only the surface charge of the adsorbent, but also the degree of ionization and speciation of the heavy metal in solution[4]. The effect of pH on copper uptake was investigated in the range of pH 2.0-6.5 and the results were presented in Fig. 1. The maximum biosorption was found to be 69.84 % for Cu(II) ions at pH 5. Therefore all biosorption experiments were carried out at pH 5. At pH range 2 to 3 the metal uptake was in the range of 22-49 %. At higher pH values the biosorption yield for Cu(II) was slightly decreased. The effect of pH on the sorption of copper(II) has been investigated by various investigators using a variety of different sorbent types. Optimum sorption capacities of copper(II) have been reported at pH values of 5.0[24,25], 6.0[26,27]. The competition of hydrogen ions for the available binding sites may result in low biosorption of copper at pH 3.0[28]. At pH values higher than 5.5 precipitation of copper was observed. Similar pH effects on copper biosorption have been reported for Papaya wood and *Penicillium simplicissimum*[29,30].
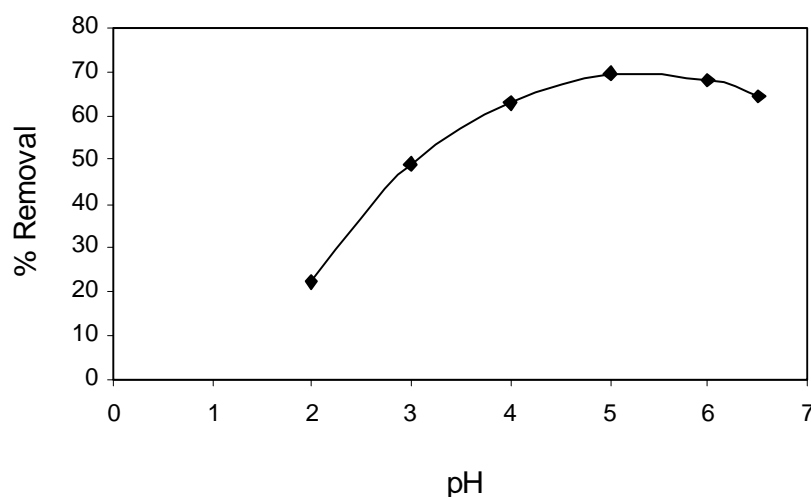

Fig. 1.   Effect of pH on copper biosorption efficiency (initial metal conc. (C_o) = 50 mg/L, m = 6 g/L, T = 25 ºC, impeller speed = 200 rpm, contact time (t) = 3 h)

Biosorbent dosage: The effect of biosorbent dosage on the biosorption of Cu(II) ions was studied using different biomass dosage in the range, 1-8 g/L as shown in Fig. 2. Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. To determine the effect of biosorbent dose, different amounts of biosorbent were suspended in 100 mL copper solution in which the concentration of copper was 50 mg/L and pH 5.0. The experiment showed that the maximum biosorption of the metal ions was attained at about biomass dosage, 6.0 g/L. When biomass concentration reaches 7 g/L a decrease is observed. This may be the result of a partial cell aggregation that occurs at high biomass concentrations as this phenomenon brings along a decrease in the number of active binding sites.
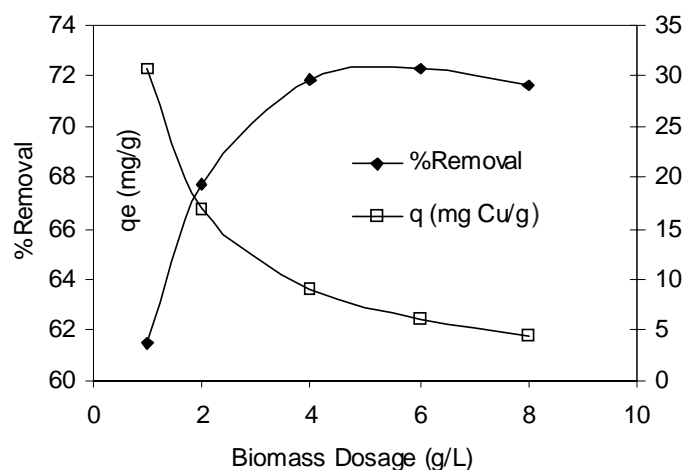

Fig. 2.   Effect of initial biosorbent concentration on biosorption capacity and the biosorption efficiency of Caucasian fir biomass

Effect of contact time: Contact time is one of the important parameters for successful biosorption application. The copper uptake by Caucasian fir at different contact times has been shown in Fig. 3. Where the adsorption rate of metal uptake was very fast, significant rate of Cu(II) removal occurred within 5 min and adsorption equilibrium was reached at 1 h. It was observed that the metal uptake of increases with very little rise in contact time up to 3 h. After this time further increase in contact time did not show an increasing in biosorption. Therefore, the optimum contact time was selected as 1 h for further experiments. This reveals the two-staged nature of sorption, the first being rapid and quantitatively predominant and the second is slower. The rapid stage is probably due to the abundant availability of active sites on the biomass and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage[29].
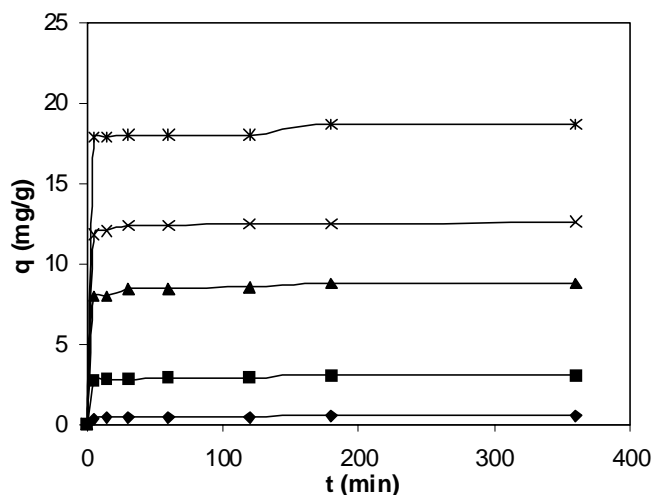
Fig. 3.   Effect of contact time on biosorption capacity (q_e mg/g biosorbent) (temperature (T) = 25 ºC, biomass dose (m) = 6 g/L, impeller speed = 200 rpm)

Equilibrium adsorption models: Adsorption isotherms express the relation between the amount of adsorbed metal ions per unit mass of biosorbent (q_e) and the metal concentration in solution (C_e) at equilibrium. Two important isotherms were used in this study *i.e.*, the Freundlich and Langmuir isotherms. The results of biosorption studies of Cu(II) at different concentrations ranging from 10 to 100 mg/L on a fixed amount of biosorbent are expressed by the above mentioned isotherms. The Langmuir model assumes that biosorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer biosorption processes. This model can be written as follows

$$q_e = \frac{(Q_{max}bC_e)}{(1+bC_e)} \tag{1}$$

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}b}\right)\frac{1}{C_e} + \frac{1}{Q_{max}} \tag{2}$$

where Q_{max} and b are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively. These constants can be determined from the linear plot of $1/q_e$ *versus* $1/C_e$.

On the other hand, the empirical Freundlich isotherm model based on a heterogeneous surface is given below:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the amount of metal sorbed by cone biomass (mg/g), C_e is the metal concentration in the solution at equilibrium (mg/L), K_f and n are Freundlich constants

characteristic of the system. K_f and n are indicators of adsorption capacity and intensity, respectively. These constants can be determined from the linear plot of log q_e *versus* log C_e.

The curves in Fig. 4 and 5 were generated from Freundlich and Langmuir model equations, respectively. As seen from Fig. 4 and 5, both the Freundlich and Langmuir adsorption models were suitable for describing the short-term biosorption of Cu(II) by Caucasian fir cones.
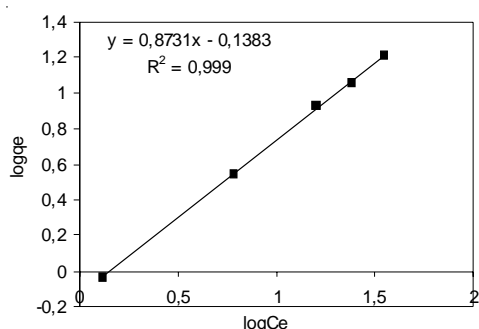

Fig. 4. Linearized Freundlich isotherm plot for biosorption of Cu(II) by Caucasian fir biomass
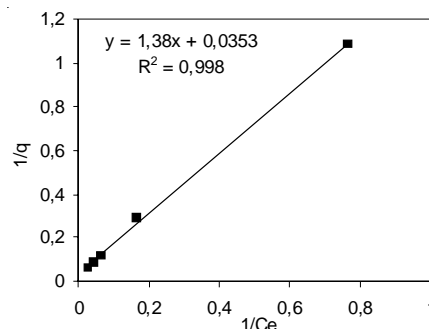
Fig. 5. Linearized Langmuir isotherm plot for biosorption of Cu(II) by Caucasian fir biomass

The Freundlich and Langmuir adsorption constants evaluated from the isotherms with correlation coefficients have been found 0.999 and 0.998, respectively. The values of K_f and n constants are 0.727 and 1.145, respectively. The values of Q_{max} and b parameters are 28.32 and 0.0256, respectively. Table-1 presents the comparison of biosorption capacity of Caucasian fir for the Cu(II) with those of various biomasses in literature[4,29,31-39]. The biosorption capacity of Caucasian fir for this metal ion is higher than that of the majority of other biomasses given in Table-1. But direct comparison is difficult due to the varying experimental conditions used in these studies.

TABLE-1
COMPARISON OF MAXIMUM BIOSORPTION CAPACITY OF CAUCASIAN FIR
FOR COPPER ION WITH DIFFERENT PLANT BIOMASSES

Adsorbent	q_{max} (mg /g)	Reference
Mimosa tannin resin	43.71	31
Apple wastes	10.80	32
Walnut shell	6.74	33
Pine bark	9.53	34
Sugar beet pulp	28.50	4
Papaya wood	19.88	29
Tectona grandis leaves	15.43	35
Carrot residue	32.74	36
Plant root tissues	0.50	37
Caucasian fir	73.80	This study
Dried Sunflower leaves	89.37	38
Rice bran	33.58	39

Effect of initial metal ions concentration on biosorption: The effect of copper(II) concentration on the sorption by Caucasian fir was investigated by varying the copper(II) concentration (10 to 100 mg/L) at a pH of 5.0, 200 rpm shaking time and 1 h contact time. Fig. 6 shows the effect of initial metal ion concentration on the adsorption of Cu(II) by cone biomass. The obtained curve showed that the biosorption efficiency decreased with the increasing of the initial concentration of the metal ions. This might be explained with the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for complexation of copper ions at higher concentration levels. The biosorption capacity, as it is a measure of the amount of metal ions bound by unit weight of biomass, first increased parallel to the increase of the initial concentration of metal ions and reached a saturation value. At higher concentrations, more metal ions are left unadsorbed in solution due to the saturation of adsorption site. When the initial copper(II) concentration shifted from 10 up to 100 g/L, the biosorption efficiency has decreased from 73.8 to 65 %.
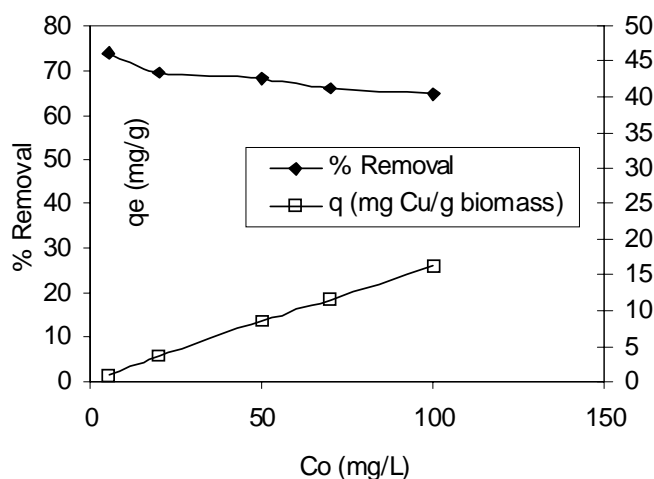

Fig. 6.   Effect of initial metal concentration on biosorption capacity (q_e mg/g biosorbent) and the biosorption efficiency of Caucasian fir biomass

Conclusion

The removal of copper ions from aquatic systems is carried out using Caucasian fir cones. The results obtained confirmed that this selected biomass exhibited high sorption capacity. The sorption performances were strongly affected by parameters such as contact time, initial copper concentration and initial pH of solution and biomass dosage. The maximum biosorption efficiency was found as 73.8 % for Cu(II) ion at the conditions of adsorbent dosage 6 g/L, pH 5, shaking time 1 h. The biosorption efficiencies were decreased with increase in initial metal concentration. The Langmuir and Freundlich adsorption model were used for modeling the

biosorption of Cu(II) ions onto Caucasian fir and was found that the adsorption equilibrium data fitted well to the both model. The study revealed that Caucasian fir could be used as a tool for the development of low-cost biomaterial-based treatment of heavy metal waste.

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