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A new biosorbent for the removal of Cu(II) from aqueous solution; red marine alga, *Ceramium rubrum*

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Abstract. Biosorption is an effective technique for the removal of heavy metals from wastewater. In this study, dried, sodium hydroxide and formaldehyde modified red alga, *Ceramium rubrum* were used for the biosorption of copper from aqueous solution. The biosorption characteristics such as pH, biomass dosage, temperature and contact time were investigated. Also, Fourier Transform Infrared Spectrophotemetric analysis of *C.rubrum* was performed to identify its structure. Langmuir and Freundlich isotherm models were applied to describe the biosorption of Cu^{2+} onto C.*rubrum* biomass at the equilibrium. Langmuir model fitted well the equilibrium data for all biosorbents. Maximum biosorption capacity of dried biomass was calculated 25.51 mg/g, while it was calculated 42.92 mg/g and 30.03 mg/g for sodium hydroxide modified and formaldehyde modified biomass, respectively. Modified biomasses have higher maximum biosorption capacities indicating that modification of biomass with NaOH and HCHOH may increase responsible active sites for biosorption on the C.*rubrum*.

Key words: Red alga; *Ceramium rubrum*, copper, atomic absorption spectrometry, isotherm, biosorption

Introduction

Heavy metals; lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe) and the platinum group elements occur as natural constituents of the earth crust and are persistent environmental contaminants since they cannot be degraded or destroyed. Toxic heavy metals in air, soil and water are global problems that are a growing threat to humanity. There are hundreds of sources of heavy metal pollution, including the mining, coal, natural gas, paper and chlor-alkali industries. Numerous processes such as ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis and electrodialysis have been used for the removal of heavy metal ions from aqueous solution (Yu, 1999).

Owing to low cost and ease of availability, compared to traditional separation methods biosorption has received considerable attention in recent years. Various species of marine alga were used as biosorbent for removal of heavy metals from environmental samples (Yu, 1999; El-Sikaily, 2007; Fagundes-Klen, 2010; Laib, 2011; Esmaeili, 2011; Nessim, 2011). But to the best of our knowledge, there is no significant study on the use of red marine alga, *Ceramium rubrum* for this purpose although there are a lot of studies on evaluation of its structure (Miller, 2002), determination of its metal content (Jordonava, 1999) and its pharmaceutical effect such as antiviral (Zagal, 2004) and antibacterial activity (Kesternich, 1997). In this study, biosorption characteristics such as pH, biomass dosage, temperature and contact time were investigated for biosorption of Cu^{2+} onto dried, sodium hydroxide and formaldehyde modified *C.rubrum*.

Materials and Methods

Apparatus and reagents

An Analytic Jena Vario 6 atomic absorption spectrometer equipped with an air-acetylene burner was used for the determination of copper. Copper hollow cathode lamp was used as the spectral radiation source. The wavelength was 324.8 nm for copper. The pH adjustment was controlled using WTW pH 720 i pH-meter.

All chemicals were of analytical-reagent grade (Merck). Distilled-deionized water was used throughout. Stock solution (1000 mg L^{-1}) of Cu^{2+} was prepared from titrisol standard (Merck) and working standard solutions were prepared fresh daily by appropriately diluting the stock solution.

Biomass preparation

The red marine alga, *Ceramium rubrum* were collected from Bosphorous, The Marmara Sea, Turkey. The fresh biomass was washed with distilled water to remove sand and other extraneous particles. This was followed by washing deionized water to release common ions such as Na^+, K^+ and Ca^{2+} present in seawater. The fresh biomass was dried in an oven at 60°C for 24 hours and dried biomass was crushed, grinded and sieved. Particle size was determined as below 60 meshes. The biomass was stored in polypropylene bottles.

Biomass modification

Accurately weighed 10 g. washed fresh biomasses were taken into a flask together with 200 mL of sodium hydroxide (0.1 M) and formaldehyde solution (2%) and left at room temperature for 76 hours. Then, biosorbents were filtered and washed with distilled and deionized water repeatedly until sodium hydroxide and formaldehyde were removed completely. The washed biomasses were dried in an oven at 60°C for 24 hours. Modified biomasses were crushed, grinded and stored in polypropylene bottles.

Batch biosorption procedure

4 g L^{-1} of biomasses at desired pH were placed in contact with 25 mL of the metal solutions in polypropylene conical flask and shaked at 350 rpm with orbital stirring. The solutions were filtered from Whatman 42 filter paper. Metal concentrations in supernatants were measured by flame atomic absorption spectrometer.

Results and Discussion

FTIR Analysis

Fig.1 shows FT-IR spectra (650-4000 cm^{-1}) curves for the dried *C.rubrum*. The main three peaks emerged at 3281.44 cm^{-1}, 1643.94 cm^{-1} and 1030.61 cm^{-1} have been assigned O-H stretching band, N-H bending band and C-O stretching band, respectively while the two peaks appeared at 1414.36 and 1222.72 cm^{-1} has been assigned S=O stretching double bands. These results exposed that *C.rubrum* have functional groups of hydroxyl, amino, carboxyl and sulfate which can act as metal binding sites and found at polysaccharides, proteins and lipid on the cell wall surface of algal biomass.

Effect of pH

To identify the most suitable pH for the effective biosorption of Cu^{2+} onto *C.rubrum*, sorption experiments were performed at different pH values in the range 3–7. The pH of solutions was adjusted with 0.1 M of HCl and 0.1 M of NaOH. Due to the formation of soluble hydroxylated complexes of the metal ions, no experiments performed at higher pH. As shown Fig.2, the maximum biosorption was occurred at pH 6 for dried (DCr), NaOH modified (NCr) and formaldehyde modified *C. rubrum* (FCr). For further experiments, the pH 6 was chosen as optimum pH.

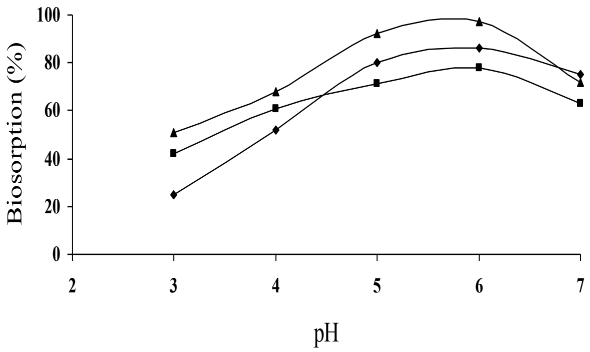

Fig. 2. Effect of pH on biosorption of Cu^{2+} onto algal biomasses (initial metal concentration: 10 mgL^{-1}; biomass dosage: $4gL^{-1}$) (▲:NCr, ◆: FCr, ■:DCr)

Effect of biomass dosage

The effects of algal biomasses dosage on the biosorption of Cu^{2+} were investigated using different biosorbent concentration in the range 2-8 gL^{-1}. At $4gL^{-1}$, quantitative results were obtained for all studied biosorbents.

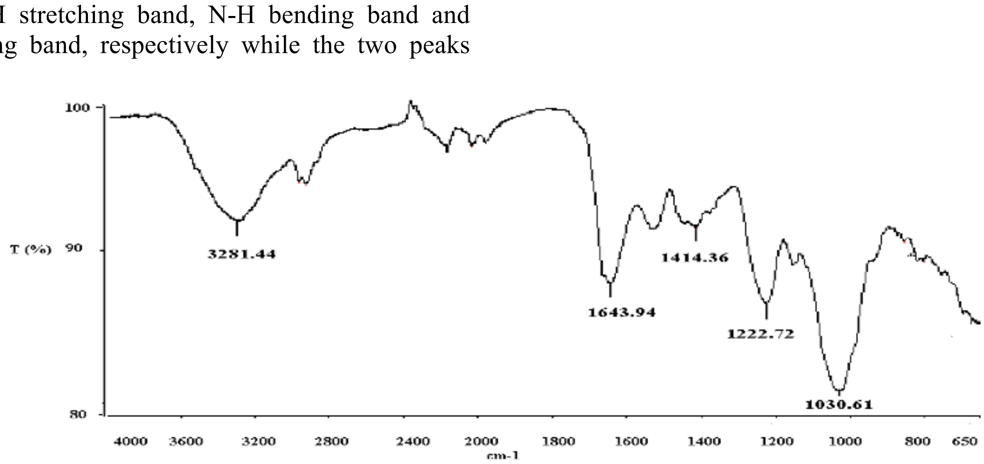

Fig. 1. FT-IR recorded spectrum for *Ceramium rubrum*

Effect of temperature

To study influence of temperature on the biosorption of Cu^{2+} onto algal biomasses, the experiments were achieved at various temperatures from 25 to 40°C. An increase in percentages of biosorption for all biomasses was observed up to 35°C and after this temperature, biosorption percentages were decreased which may be due to the damage of active binding sites. As a result, the optimum temperature was selected 35°C for further experiments.

Effect of contact time

The effect of contact time on the biosorption was investigated using different contact time between 15-180 minutes. As can be seen Fig. 3, the biosorption increased with rise in contact time up to 90 min and after then it was almost constant. Since the equilibrium occurred at 90 min, it was selected as optimum contact time.

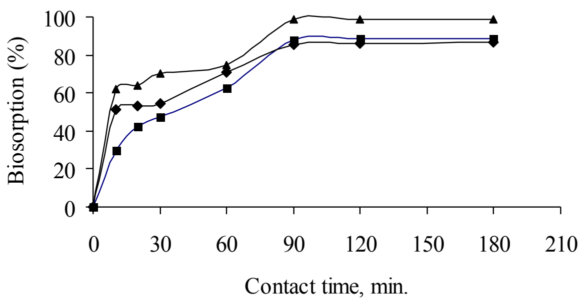

Fig. 3. Effect of contact time on biosorption of Cu^{2+} onto algal biomasses (initial metal concentration: 250 mgL^{-1}; biomass dosage: $4gL^{-1}$) (▲:NCr, ◆: FCr, ■:DCr)

Equilibrium isotherm models

Two main adsorption isotherm models which are namely Langmuir and Freundlich were applied to describe the biosorption of Cu^{2+} onto all algal biomasses. The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate adsorbed on an adsorbent as a function of concentration at a given temperature and assumes that monolayer biosorption occurs at homogeneous sites on the biosorbent. The equation of this model can be written as follows (Sari, 2008)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (1)$$

where qe is the concentration of metal ion on biosorbent at equilibrium (mg/g), Ce is the concentration of metal ion in the solution at equilibrium (mg/L), qm is the maximum biosorption capacity of biosorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg).

The Freundlich isotherm model assumes that non-ideal and multilayer sorption occurs at heterogeneous surfaces of the biosorbent. The Freundlich model is

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity which varies with the heterogeneity of the material.

Table 1 shows maximum biosorption capacities (qm), correlation coefficients (R^2) and the biosorption constants (K_L, K_F and n) resulting from equilibrium biosorption studies of Cu^{2+} onto *C.rubr*um biomasses. The correlation coefficients were found to be 0.993, 0.991 and 0.991 for dried, NaOH modified and formaldehyde modified *C. rubrum* respectively indicating that the biosorption of Cu^{2+} onto *C.rubrum* biomasses fitted well the Langmuir model. Modified biomasses have higher maximum biosorption capacities indicating that modification of biomass with NaOH and HCHOH may increase responsible active sites for biosorption on the C.*rubrum.* The values of *1/n* calculated from Freundlich isotherm equation were found to be 0.58, 0.81 and 0.54 for DCr, NCr and FCr, respectively. The *1/n* values were in the range of 0-1, indicating that the biosorption of Cu^{2+} onto *C.rubrum* biomasses was favourable at studied conditions.

Table 1. Comparison of Langmuir and Freundlich constants and max. biosorption capacities

Model	Bisorbent	qm (mg/g)	K_L (L/mg)	R^2
Langmuir	DCr	25.51	0.13	0.993
	NCr	42.92	0.03	0.991
	FCr	30.03	0.09	0.991
		K_F	**1/n**	**R^2**
Freundlich	DCr	3.06	0.58	0.947
	NCr	2.31	0.81	0.988
	FCr	2.75	0.54	0.989

Conclusion

Depending on the results, *Ceramium rubrum* can be used as an effective biomass for the removal of Cu^{2+} from wastewater in terms of high biosorption capacity, ease of availability and low cost.

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