

Full Length Research Paper

Evaluation of the activated carbon prepared from the algae *Gracilaria* for the biosorption of Cu(II) from aqueous solutions

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The batch removal of copper (II) ions from aqueous solution and wastewater using the activated carbon prepared from *Gracilaria* by acid decomposition was investigated. The effect of pH, biosorption time, adsorbent dose, and metal ions concentration, were considered. The most effective pH was found to be 4.0. The biosorption capacities were solution pH dependent and the maximum uptake for copper with initial concentration 70, 100 and 150 mg l⁻¹ at pH 4.0 were obtained 95.53, 93.72 and 88.84%, respectively. The total metal ions biosorption occurs within 2 h. The equilibrium adsorption data fitted to Langmuir and Freundlich isotherm models. Both the models represent the experimental data satisfactorily. The adsorption follows second order kinetic. This study shows the benefit of using activated carbon from marine red algae as a low cost sorbent for the removal of copper from aqueous solution wastewater.

Key words: Biosorption, copper, *Gracilaria*, wastewater, activated carbon, isotherm model.

INTRODUCTION

Heavy metal pollution corresponds to an important environmental problem due to its toxic effects and cummulation throughout the food chain and consequently in the human body (Kowalski, 1994). Copper (II) is recognized to be one of the heavy metals most wide spread heavy metal contaminants of the environment (Ho and Mckay, 2003). The main treatment processes for the removal of metal ions include evaporation, chemical precipitation, membrane separation, adsorption and ion exchange processes which are being used to remove copper (II) from wastewater (Mckay, 1995). However, these technologies are most appropriate in situations where the concentrations of the heavy metal ions are comparatively high. When the concentration of the heavy metals in the wastewater is low, these techniques are either ineffectual or costly.

Activated carbon has unquestionably been the most popular and widely used adsorbent in wastewater treatment employments throughout the world. However,

activated carbon remains a costly material since the higher the quality of the activated carbon, the greater will be its cost (Babel and Kurmiawan, 2003). Therefore, searching for a low cost activated carbon and other adsorbent materials is of great importance for the wastewater treatment (Fourrest and Roux, 1992; El-Sikaily et al., 2006; Abdelwahab et al., 2006; Karadag, 2007).

The goal of present work was to test the ability of an activated carbon from *Gracilaria* to remove copper (II) ions from aqueous solution. In addition, the kinetics, equilibrium isotherm, retention time, pH, initial concentration and dosage of biosorbent were also investigated.

MATERIALS AND METHODS

Preparation of biomass

The biomass used was the red seaweed *Gracilaria*. It was collected from the Persian Gulf on Queshm Island. Before use, it was washed several times with tap water to remove the sand particles and dirt. Then clean alga was sun dried for 5 days. Dry biomass was milled and an average of 0.5 mm particles was used for biosorption experiments.

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Activated carbon

The dried red alga *Gracilaria* 112 g was added in small portion to 90 mL of 97% H₂SO₄ and the resulting mixture was kept for 24 h at room temperature followed by refluxing in fume hood for 4 h. After cooling, reaction mixture was washed repeatedly with deionized water and soaked in 2% NaHCO₃ solution to remove any remaining acid, and when the pH of the activated carbon reached 7, it was dried in an oven at 150°C for 46 h.

Chemicals

Stock copper solution (180 mg l⁻¹) was prepared by dissolving 0.353 g of copper sulfate pentahydrate (Merck) in 500 ml of deionized water. Copper solutions of different concentration (50-180 ppm) were prepared by adequate dilution on the stock solution with deionized water. The initial pH is adjusted with 1 M HCl or 1 M NaOH. The effect of pH on the equilibrium adsorption was investigated by employing concentration of Cu(II) (50 mg l⁻¹) and 2 g activated carbon.

The suspensions were shaken at room temperature (23 ± 2°C) using agitation speed (300 rpm) for 2 h. Adsorption of Cu(II) was studied using different dosages of activated carbon in 30 ml solution of 50, 70, 100, 130, 150, 180 mg l⁻¹ of initial Cu(II) concentration and initial pH 4.0. Initial and final concentrations of metal ions in the solution of each flask were measured by atomic adsorption spectroscopy (GBC-932).

RESULTS AND DISCUSSION

Effect of pH on biosorption

The pH of the aqueous solution is an important controlling parameter in the adsorption process (Asmal et al., 1998). The effect of pH on copper biosorption on activated carbon was studied at room temperature by varying the pH. The uptake of copper (II) showed an increase with an increase in pH from 1.0 to 4.0. The uptake of Copper (II) in pH 1, 2, 4, 5 and 6 were obtained 75.68, 93.40, 97.62, 86.33 and 81.47%, respectively. The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes. Because of this effect at higher pH values, ligands such as carboxylate and sulfonate groups could take up fewer metal ions (Kalyani et al., 2004).

The effect of biosorption time

The uptake of Cu(II) ions increased quickly, and after 15 min, the change becomes slow. However, an increase in retention time from 15 to 120 min resulted in a decrease in the remaining concentration of heavy metals. The uptake of copper (II) with 50, 70, 100, 130, 150 and 180 mg l⁻¹ concentrations was 58.54, 53.76, 51.51, 48.43, 40.19 and 35.64%, respectively, at 15 min, 79.91, 76.52, 72.89, 69.06, 66.63 and 51.61%, respectively, at 60 min, and 93.99, 95.53, 93.72, 93.04, 88.84 and 85.49%, respectively, at 120 min.

Effect of adsorbent dose on biosorption

Different dosage of biosorbent did not have an effect on the results, but the 5 g of biosorbent showed higher uptake. Therefore this result was anticipated because increasing adsorbent doses provides greater surface area.

Effect of metal ion concentration on biosorption

By increasing initial concentration, the uptake was decreased. This was due to the saturation of the sorption sites on adsorbents the maximum uptake for copper with initial concentrations of 70, 100, 150 mg l⁻¹ at pH 4.0 were 95.53, 93.72 and 88.84%, respectively.

Equilibrium studies

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption give the capacity of adsorbent. It is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium (Han et al., 2005). In order to investigate the adsorption isotherm, two equilibrium models, Langmuir and Freundlich, were analyzed.

Langmuir isotherm

The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm can be represented as (Langmuir, 1916).

$$q_e = b \cdot q_{\max} \cdot C_e / (1 + b \cdot C_e) \quad (1)$$

Where q_e is the amount of metal ion adsorbed (mg g⁻¹), C_e is the equilibrium concentration (mg L⁻¹), q_{\max} is the maximum adsorption capacity and b is an affinity constant.

Freundlich isotherm

The empirical Freundlich equation based on a monolayer

Table 1. Isotherm parameters obtained for biosorption of copper using activated carbon.

Isotherm model	Activated carbon		
	2 g	3 g	4 g
Langmuir			
Q _m (mg g ⁻¹)	2.527	1.817	1.330
b (L mg ⁻¹)	0.208	0.493	0.646
R ²	0.997	0.993	0.999
Freundlich			
n	2.444	2.704	2.633
K _F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	0.640	0.671	0.475
R ²	0.992	0.995	0.974

Table 2. Parameters obtained for first and second-order kinetic model.

Activated carbon	Initial Cu concentration (mg L ⁻¹)	First-order kinetic model		Second-order kinetic model	
		k ₁	R ²	k ₂	R ²
2 g	50	0.003	0.916	3.511	0.995
	70	0.003	0.934	3.449	0.989
	130	0.002	0.997	6.816	0.973
	150	0.002	0.983	4.550	0.983
	180	0.003	0.999	5.491	0.870

adsorption by the adsorbent with a heterogeneous energy distribution of active sites is given below by Eq (2):

$$q_e = K_f \cdot C_e^{1/n} \quad (2)$$

Where K_f and n are the Freundlich constants (Freundlich, 1906). The results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherm. These isotherm constants for Cu(II) are presented in Table 1.

Adsorption kinetics studies

The kinetic of adsorption describes the rate of copper ions uptake on activated carbon which controls the equilibrium time. The adsorption kinetics of Cu(II) biosorption on algae follows second order rate expression given by:

$$dq_t / dt = K_2 (q_e - q_t)^2 \quad (3)$$

Where K₂ is the equilibrium rate constant (g/mg min). q_e and q_t are the sorption capacity at equilibrium at time t.

The integrated form of Eq (3) becomes:

$$1/(q_e - q_t) = 1/(q_e) + K_2 t \quad (4)$$

This has linear form:

$$t/q_t = 1/K_2 \cdot q_e^2 + (1/q_e) t \quad (5)$$

A plot t / q_t versus t indicate a straight line of slope (1/q_e) and an intercept of (1/K₂ · q_e²) (Ag and Aktay, 2002; Khezamia and Capart, 2005). This isotherm constants are presented in Table 2. These results suggest that the sorption of Cu(II) ions followed the second-order kinetic model, which relied on the assumption that biosorption could be the rate-limiting step.

Conclusion

In this study, adsorption of Cu(II) on activated carbon prepared of alga (*Gracilaria*) was investigated. The data obtained through this work support the view that the activated carbon is an effective low cost adsorbent for the removal of copper from aqueous solution. The adsorption of metal ions is dependent on the amount of activated carbon, concentration of metal ion, and retention time

and pH of the metal solution. Maximum removal of copper on activated carbon is at pH 4.0. The equilibrium adsorption data are correlated by Langmuir and Freundlich isotherm equation.

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