

Biosorption of Copper Ions by Marine Brown Alga *Fucus vesiculosus*

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ABSTRACT

Copper is present in different types of industrial effluents, being responsible for environmental pollution. Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. The biomass of marine algae has been reported to have high uptake capacities for a number of heavy metal ions. In this paper, the adsorption properties of a pre-treated biomass of marine algae *Fucus vesiculosus* it was collected near Bushehr, Persian Gulf in Iran, for Cu (II) were investigated. Equilibrium isotherms and kinetic studies were carried out for the biosorption of Cu (II) ions from aqueous solution using the algae brown biomass from batch adsorption experiments. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were applied to describe the biosorption of the Cu (II) ions onto *FV* biomass. The equilibrium time was about 340 min and the adsorption equilibrium data were well described by the Langmuir's equation. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The maximum adsorption capacity has been extrapolated to 1.85 mmol g⁻¹. All these observations indicate that the Copper biosorption on *FV* is mainly based on ion exchange mechanism and this biomass could be then a suitable sorbent for the removal of heavy metals from wastewaters. This study demonstrated that the biomass of *FV* could be used as an effective biosorbent for the treatment of Copper (II) containing wastewater streams.

Keywords: Copper; *Fucus vesiculosus*; Biosorption; pollution; adsorption isotherm

INTRODUCTION

Many industries such as electroplating and metal finishing discharge heavy metal-laden effluents into the environment, being one of the major contributors to heavy metal pollution in surface waters (Davis A. et al 2003). Heavy metal pollution is a major environmental concern in many countries. Several methods are used to remove toxic metals from industrial effluents, such as precipitation (Rebhun and Galil, 1990), oxidation/reduction (Brewster M.D and Passmore R.J, 1994), artificial membranes (Kurt and Volchek, 1996), ion exchange (Marcus and Kertes, 1969) and evaporation are extremely expensive or inefficient for metal removal from diluted solutions containing from 1 to 100 mg/L of dissolved metal. Physico-chemical methods are currently used to remove metals from liquid effluents (Suderman W. and Oskarson A, 1991), but these methods have important disadvantages, such as unpredictable metal ion removal, high reagent requirements, and the generation of toxic sludge which are often difficult to dewater and also require extreme caution in their disposal (Kapoor et al. 1999). Cost effective technologies or sorbents for treatment of metal contaminated waste streams are needed (Bailey et al. 1999). Alternative metal removal and/or recovery methods being considered are based on metal-sequestering properties of certain natural materials of biological origin (Valentine et al. 1996; Di Simine et al. 1998; Kumar et al. 2010). Biosorption is a term that describes the removal of heavy metal, by the passive binding to non-living biomass from an aqueous solutions. Biosorption uses inexpensive dry biomass to extract industrial effluents of toxic heavy metals. The biosorption is a process in which solids of natural origin are employed for binding heavy metals. The biomass can be composed of algae, mosses, fungi, bacteria, and various plant species. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. The alga can be collected and/or cultivated in many parts of the world, factor that has encouraged the development of new biosorbent materials using biomass. The toxic effects of Copper on microorganisms are well documented and many reports exist of Copper uptake by microorganisms (Romera et al. 2008; Holan and Volesky 1994; Sheng et al. 2004). Copper, like the majority of heavy metals, is toxic but it has been widely used in metallurgical and tanning industries. Therefore, this work was developed with the objective of evaluated the Copper biosorption process by means of the seaweed *Fucus vesiculosus*. The objective of the present study was investigate the use of *FV* biomass as a biosorbent for the removal of Cu (II) from aqueous solution and also the effects of initial metal ion concentration, contact time, concentration of algal biomass and pH.

MATERIALS AND METHODS

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Biomass

The biomass of *Fucus vesiculosus* (*FV*) was used in this work: it was collected on the near Bushehr, Persian Gulf in Iran. Collected seaweed samples were washed with tap water to remove sand and epiphytes and then rinsed thoroughly in deionised water. After drying at 60°C for 12 hours, the algae were crushed, sieved, and the 0.355–0.5 mm particle size fraction was kept for the experiments. This fraction used as biosorbent for Copper. The tests were carried out at the chemical laboratory of the Ilam University since April to September 2010. Once the selected fraction, determination of elemental composition and the extent of the apparent density and ash content were made. (Table.1)

Table 1. Elemental composition and density of *Fucus vesiculosus*

	<i>Fucus vesiculosus</i> (0.355 < d < 0.500) mm
C (%)	40,0
N (%)	2,0
H (%)	5,0
O (%)	41,5
S (%)	0,5
Bulk density (kg/m ³)	820
Ash (%)	11

Copper solution and AAS Measurements

Copper solutions with different initial concentrations were prepared by dissolving CuCl₂·6H₂O in company Merck in deionized water. Solutions of NaOH (1 M) and HCl (1 M) were used for pH adjustment. For metal concentration measurements, after each test or biosorption experiment, the liquid phase was separated from the adsorbent by a filtration system using 0.45 μm membranes. An, atomic absorption spectrometer (Chem., Tech, Analytical CTA 2000) was used.

Surface characterization

FT-IR analysis of dried activated algae was determined as follows: KBr pellet was prepared. The infra-red spectra were collected by FT-IR within the range 400 to 4000 cm⁻¹.the spectrum analysis was realized as previously described (Guibaud et al. 2003) The BET surface and the porosity were determined using the methods proposed Kardirvelu and co-workers(Kardirvelu et al. 2000)

Kinetic and isotherm test

The isotherm experiments were carried out in bottle flasks filled with 1000 ml of water thoroughly mixed with 0.08 g of *FV* at 25 ± 1°C. The initial concentrations of metal ions were ranged from 0.01 to 0.40 mmol / L. The initial pH was measured and if necessary, NaOH or HCl solution was added to reach an initial pH close to 5.5. To obtain the kinetic curves, 0.08 g of *FV* were introduced in 1000 ml of metallic solution, at pH 5.5 and 20 °C, with an initial concentration ranged between 4 and 7.10⁻⁵ M. After the introduction of the metal ions, samples were collected at suitable time intervals, filtered through a 0.45 μm cellulose acetate membrane filter, and then analyzed for metal and calcium elements with an atomic absorption spectrophotometer (Chem., Tech, Analytical CTA 2000).

The equilibrium data were analyzed in accordance with the Langmuir sorption isotherm. (eq.1):

$$qe = \frac{q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e}$$

Where q_{\max} (mmol/g of dry weight) is the maximum uptake capacity corresponding to complete monolayer coverage, C_e (mmol/L) the equilibrium solute concentration, and b the equilibrium constant related to the energy of adsorption (L/mmol).

Linear form equation, on rearrangement to a linear form, a plot of $1/q_e$ against $1/C_e$ gives a straight line. (Eq.2):

$$\frac{1}{q_e} = \frac{1}{b_L q_m C_e} + \frac{1}{q_m}$$

The empirical Freundlich equation based on sorption on a heterogeneous surface is given by Equation (Eq.3):

$$qe = K_F C_e^{1/n_F}$$

Where K_F is the Freundlich constant ($L^{1/n} \text{ mmol}^{1-1/n} \text{ g}^{-1}$) and $1/n_F$ the Freundlich parameter. Both models were developed for a single-layer adsorption, but the Freundlich isotherm provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. This model is more general than the Langmuir, since it does not assume homogeneous surface or constant adsorption energy for each site.

RESULTS

Specific surface area characterization

The BET surface determination and the mercury porosity results (table 2) show that the *FV* is not conversational porous material because of its very low BET surface values. However, the water immersion leads to an increase of this specific area and a same tendency was observed for the total intrusion volume and the medium pore diameter. It can be concluded that the contact with bent structure. This feature could be interesting for an application in water treatment.

Table 2. Comparison of surface properties of *Fucus vesiculosus* before and after immersion in water

	<i>Fucus vesiculosus</i> before water immersion	<i>Fucus vesiculosus</i> after water immersion
Total intrusion volume	0.028 mLg ⁻¹	0.085 mLg ⁻¹
Medium pore diameter	6125 nm	16521 nm
BET surface area	0.19± 0.3 m ² g ⁻¹	1.82± 0.21 m ² g ⁻¹

Determination of chemical surface groups with FT-IR

FTIR spectroscopy has been frequently used to detect vibrational frequency changes in seaweeds (Park et al. 2004; Sheng et al. 2004). The FT-IR analysis was used for detecting vibration frequency changes of native moieties in the algal sorbent. It is well known that the cell wall composition of algal biomass contains a large number of complex organic components such as proteins, lipids, carbohydrate polymers (cellulose, xylane, mannan, alginic acid) and inorganic ions (Ca^{2+} , Mg^{2+}) (Davis et al. 2003). Numerous chemical groups have been proposed to be responsible for the biosorption of metals by macroalgae.

The most specific peaks are the following: 1744 and 1729 cm^{-1} bands correspond to the free C=O, 1525 and 1511 cm^{-1} band is vibration amide groups, 1370 and 1378 cm^{-1} band correspond to $-\text{SO}_3$, 1205 and 1210 cm^{-1} band are the vibrations of carboxyl groups, and 1029 cm^{-1} band is vibration alcohol groups. (Fig 1) Moreover, the carboxylic, carboxylate and phosphate groups in the cell wall are functional groups with acid/base properties, and could directly affect the adsorption capacity of the biomass in relation with the pH in solution.

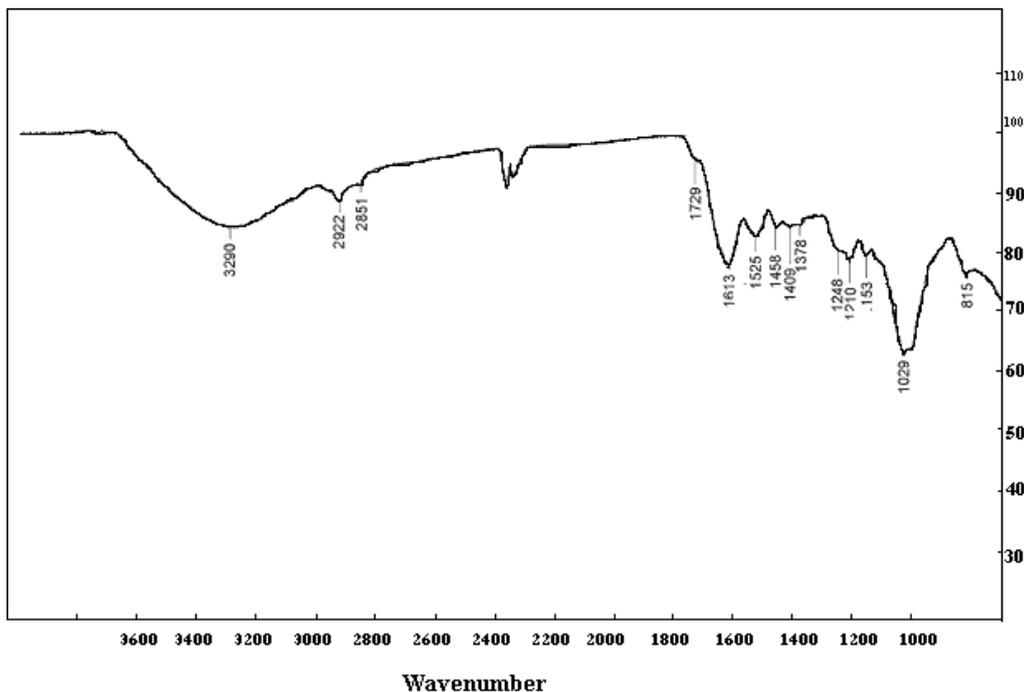


Figure 1. Infrared spectra Cu- Loaded *Fucus vesiculosus*

Kinetic experiments

Figure 2 shows the kinetics of metal adsorption onto the algae brown *FV* biomass, at 25 °C, pH 5.5, in deionized and tap water, the contact times to reach the mass balance were obtained at 340 min. This time obtained by batch reactor studies. Moreover, for similar experimental conditions, a light reduction in the Cu fixation capacity was observed in the case of tap water and probably due to a competition of fixation between the ions initially present in this natural water and Cu (II).

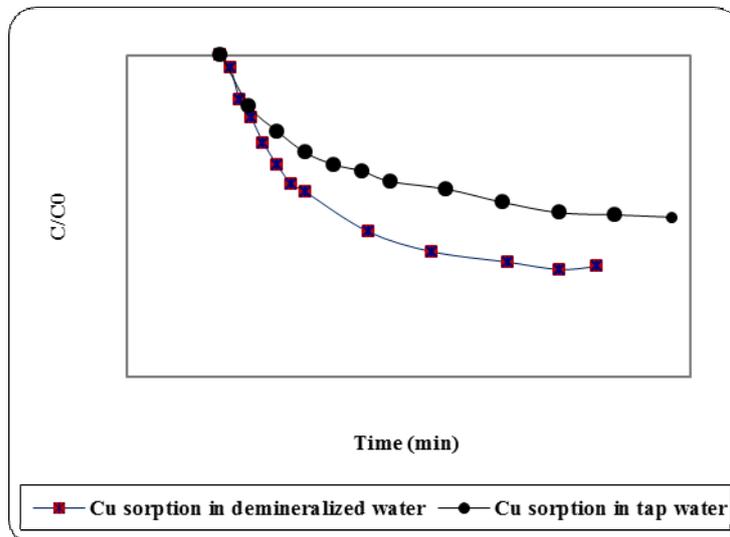


Figure 2. The adsorption kinetic of a Copper at pH 5.5 and 25°c. In demonized water (■) and in tap water (●).

Adsorption isotherm curves

Equilibrium sorption studies were performed to provide the maximum metal adsorption capacities of *FV* biomass. Adsorption isotherm curves were performed under constant solution pH values of 5.5. The Copper fixation curve obtained in deionized water presents a favorable and important ion sorption onto the *FV* (Fig.3).The Langmuir model gives a better description of the experimental data ($r^2 = 0.993$) than the

Freundlich equation ($r^2 = 0.978$) and a maximum fixation capacity is deduced to 1.85 mmol g^{-1} . (Table 3) To investigate the use of *FV* under natural conditions, the same experiment was carried out in tap water and the results are also presented. Experimental fixation capacities obtained in tap water are much less described by the tested models and show a decrease in comparison with deionized water. The difference could be attributed to a competition mechanism between ions naturally present in tap water and Copper, for the binding moieties present onto *FV* surface. As far as calcium ions are concerned, an average concentration of 47 mg L^{-1} is given for example in tap water. Nevertheless a theoretical fixation capacity can be estimated close to 1.85 mmol/g with the Langmuir model. A comparison of these results with adsorption capacities reported for other adsorbents (algae, microorganisms, agricultural wastes, activated carbons, and commercial cations exchange resins) is given in Table 4. It can be concluded that brown algae in general and especially *FV* presents high biosorption capacities for Copper, since the value is very similar than those of commercial ionic exchanger resins.

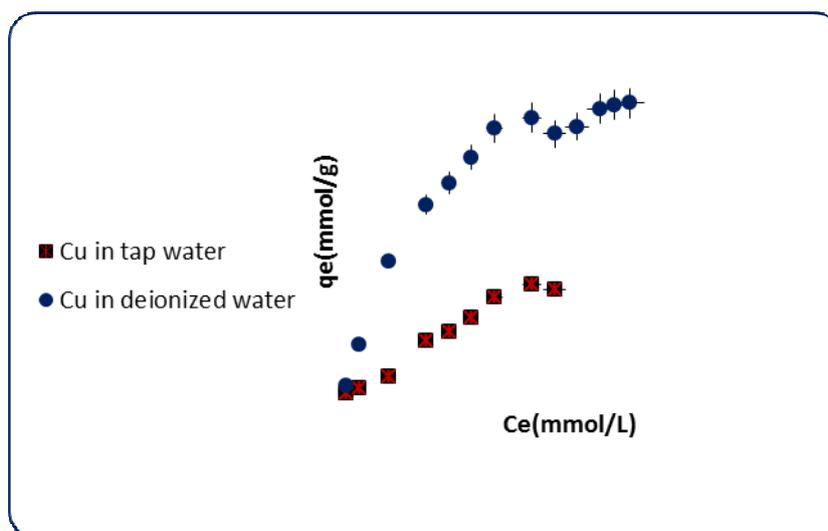


Figure 3. Sorption isotherm of a Copper in demonized water (●) and in tap water (■).

In this represents the Langmuir fit (rang concentration; 0.11 to 0.21 mmol L^{-1} for demonized water and 0.009 to 0.111 mmol/g for tap water, $\text{pH}=5.5$, dry *Fucus vesiculosus* concentration 0.08 mg L^{-1})

Table 3. Calculated parameters from Langmuir and Freundlich equations (q_m in mmol g^{-1} , b_L in L mmol^{-1} , K_F in $\text{L}^{1/n} \text{mmol}^{1-1/n} \text{g}^{-1}$)

Copper biosorption in deionized water		Copper biosorption in tap water	
Langmuir	Freundlich	Langmuir	Freundlich
$q_m = 1.85$	$K_F = 2.544$	$q_m = 1.72$	$K_F = 2.305$
$b_L = 21.55$	$1/n_F = 0.438$	$b_L = 8.460$	$1/n_F = 0.669$
$r^2 = 0.996$	$r^2 = 0.978$	$r^2 = 0.957$	$r^2 = 0.968$

Table 4. Comparison of various literature studies of Copper removal by biosorption.

	Species	pH	Ion	Capacities(mmol/g)	References
Alga browns	<i>Fucus vesiculosus</i>	5.5	Cu^{2+}	1.85	This work
	<i>Cymodocea nodosa</i>	4.5	Cu^{2+}	0.83	Sanchez <i>et al.</i> , 1999
	<i>Fucus serratus</i>	5.5	Cu^{2+}	1.73	Ahmady-asbchin <i>et al.</i> , 2008
	<i>Sargassum vulgare</i>	4.5	Cu^{2+}	0.93	Davis <i>et al.</i> 2003
	<i>Sargassum fluitans</i>	4.5	Cu^{2+}	0.80	Davis <i>et al.</i> 2000
	<i>Laminaria japonica</i>	4.5	Cu^{2+}	1.59	Fourest and Volesky, 1997
Alga green	<i>Sargassum sp.</i>	5.0	Cu^{2+}	0.99	sheng <i>et al.</i> , 2004
	<i>Codium vermilara</i>	6.0	Cu^{2+}	0.27	Romera <i>et al.</i> 2007
	<i>Spirogyra insignis</i>	6.0	Cu^{2+}	0.30	Romera <i>et al.</i> 2007
Alga red	<i>Ulva sp.</i>	5.0	Cu^{2+}	0.75	Sheng <i>et al.</i> 2004
	<i>Chondrus crispus</i>	6.0	Cu^{2+}	0.64	Romera <i>et al.</i> 2007
Fungus	<i>Palmaria palmata</i>	6.5-7	Cu^{2+}	0.10	Pracher <i>et al.</i> 2004
	<i>Aspergillus armata</i>	6.0	Cu^{2+}	0.33	Romera <i>et al.</i> 2007
	<i>Aspergillus niger</i>	5.0	Cu^{2+}	0.24	Dursun <i>et al.</i> , 2003

Sorption mechanisms

The adsorption kinetic study has highlighted an ion exchange mechanism responsible for metal uptake. The release of calcium, initially fixed onto the *FV*, has been followed in the same time of Copper adsorption. This release depends on the initial Copper concentration of the solution, which could lead to a fixation mechanism by ion exchange. Because the isotherms of Cu^{2+} adsorption and Ca^{2+} desorption were practically similar, Cu^{2+} ions seemed to be exclusively adsorbed by an ion exchange mechanism. Ion-exchange is an important in biosorption, because it explains many of the observations made during heavy metal uptake experiments. Under certain conditions, the ions attracted to a solid surface may be exchanged with other ions in an aqueous solution. Both cations and anions exchange can occur, but in some natural material, cations exchange is the dominant process.

DISCUSSION

Our results suggest that *Fucus vesiculosus* biomass could be an interesting low-cost biosorbent for Cu^{2+} removal from aqueous solutions. The experimental data in deionized water well describes by the Langmuir model. A comparison of the biosorption capacity with other sorbents reported in previous studies for the adsorption of Cu^{2+} ions also shows that the *FV* is more efficient for this purpose. The surface structure of biosorbent is modified by water. Physico-chemical investigations indicate the presence of at least sulfur or phosphates, carboxylic acid, amine and phenol moieties. A large number of acidic functional groups at the surface lead to a high value of total proton exchange capacity and a Copper uptake by cationic exchange mechanism. Interesting Copper fixations in natural water have been obtained and authorize promising further applications at pilot scale.

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