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Copper Removal from Aqueous Solutions Using Macro Alga (*Ulva lactuca*): Equilibrium and Kinetic Studies

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The removal mechanism of Cu^{2+} from aqueous solutions using a dried and untreated macro algae species (*Ulva lactuca*) as the adsorbent was investigated. The equilibrium data obtained from the adsorption of the metal ions was in good accordance with the Langmuir isotherm and the maximum adsorption capacity (Q_m) was calculated as 38 mg/g. Lagergren pseudo-first order and pseudo-second order reaction rate equations were used to calculate adsorption rate of copper. Best model of copper adsorption rate was as determined pseudo-second order rate model.

Key Words: Biosorption, Copper, Heavy metals, Macro alga, *Ulva lactuca*.

INTRODUCTION

Copper is one of the heavy metals that are present in the wastewaters of electroplating and dyestuff industries and it causes highly toxicological effects at high concentrations in the aquatic areas[1]. Receiving environment limit values have been determined for such heavy metals in resources in which the water quality classification has been carried out by the national and the international authorities[2,3]. Although, not causing significant problems at low concentrations, copper has been reported to bring forth undesirable ecological effects at concentrations higher than 0.2 mg/L[4]. Biosorption is a cheap, clean and an efficient process that removes several types of contaminants from aqueous solutions using waste or commercially invaluable materials. In the past ten years, many different types of material including waste sludge[5], fly ash[6], pine bark[7], orange wastes[8] have been used as the adsorbent. However, it was observed that the studies were mainly concerned with the use of bacteria, algae, fungi and yeasts[9]. Extensive dispersion of the green algae *Ulva lactuca* in the seas makes it an easily accessible and low cost adsorbent[10]. The studies that were conducted using untreated (such as acid/base processes, high temperature heat treatments) *Ulva lactuca* were reported less in literature. In this study, the adsorption characteristics of untreated *Ulva lactuca* has been investigated in understanding the biosorption of Cu^{2+} ions from aqueous solutions.

EXPERIMENTAL

Prepration of the adsorbent: *Ulva lactuca*, which has a wide area of dispersion starting from the shores in the Marmara Sea, has been collected along the sea side and after it has been brought to the laboratory, it has been repeatedly washed with tap water and later with de-ionized water in order to get rid of the inert materials and the ions present in the sea water (Ca^{2+}, Na^+ *etc*.). The washed *Ulva lactuca* has been dried in an incubator at a controlled temperature (at 50 ºC) to lose its water content (without causing any changes in the distribution of the functional groups, density or the acidic properties) and has been converted into powder form in a commercial grinder (mean particle size distribution 8-10 µm). The copper used in the study has been analytical grade $Cu(NO_3)_2 \cdot 2H_2O$ purchased from Sigma Chemical Co., USA. The residual metal analysis has been carried out using a Perkin-Elmer AAS Atomic Absorption Spectrometer. All experimental work has been carried out in triplicates and after statistical evaluation of the results, the average values were reported.

Batch experiments: The pH adjustments of the metal solutions have been done using 1 mol/L NaOH as the base and HNO_3 as the acid. All the experiments were carried out at 20 ± 1 ºC. At the predetermined experimentals conditions, samples were centrifuged and supernatant was determined using a atomic absorption spectrometer.

Adsorption isotherms: Two fundamental models, namely the Langmuir isotherms[11] and the Freundlich isotherms[12] have been used to fit the experimental data. The Langmuir equality can be written in the form that has been stated below:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

here, C_e is the equilibrium concentration (mg/L); q_e is the amount of adsorbed metal ions (mg/g); Q_m is the maximum metal adsorption per gram of adsorbent; and K_a was the adsorption equilibrium constant (L/mg). The Freundlich isotherm could be given in the form below:

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

K_F and 1/n Freundlich are the model constants indicating the relative adsorption capacity of the adsorbent (mg/g) and the adsorption density, respectively.

Adsorption kinetics: As in many studies reported in the literature, the kinetic evaluation of the biosorption of Cu^{2+} using *Ulva lactuca* has been carried out by the Lagergren pseudo-first order and pseudo-second order reaction rate equations[13-15]. The Lagergren pseudo-first order rate equation is given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

here, the amount of Cu^{2+} adsorbed on the adsorbent at a particular time t, q_t (mg/g), is the Lagergren adsorption rate constant k_1 (1/min). The kinetic data has also been studied using a further analysis method, the pseudo-second order rate equation.

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_{eq}^2}\right] + \frac{1}{q_{eq}} t \quad (4)$$

here k_2 the pseudo-second order adsorption rate constant (g/mg min) and the second order reaction rate equation have been used. q_e could be obtained from the slope of the line and k_2 could be obtained from the intersect.

RESULTS AND DISCUSSION

Characterization of *Ulva lactuca*: The FT-IR spectrum analyses regarding *Ulva lactuca* are given in Table-1. The comparison of the dominant peak analyses of the FT-IR spectra of the natural and copper loaded *Ulva lactuca* display significant changes. The significant changes observed in the wave numbers of the specific peaks of the hydroxyl, amine, carboxyl acid and phosphate groups as seen in Table-1.

TABLE-1
FT-IR SPECTRUM ANALYSIS OF *Ulva l.*

Functional groups	*Natural alga*	*Cu loaded alga*
	Carboxylic acid	
O-H stretching	2933	2923
C-O stretching	1259	1223
	Amine	
N-H stretching	3444	3436
N-H bending	1666	1661
C-N stretching	1384	1364
	Phosphate	
P-O stretching	1058	1035

Effect of contact time: The Cu^{2+} adsorption efficiency of *Ulva lactuca* at varying initial metal concentrations between 10 and 150 mg/L depending on the duration of contact could be seen in Fig. 1. The adsorption efficiency of the metal ions was observed to increase with increasing contact time. The rate of adsorption is reasonably high during the first 20 min of adsorption and at the end of 1 h of stirring, 90 % of the metal

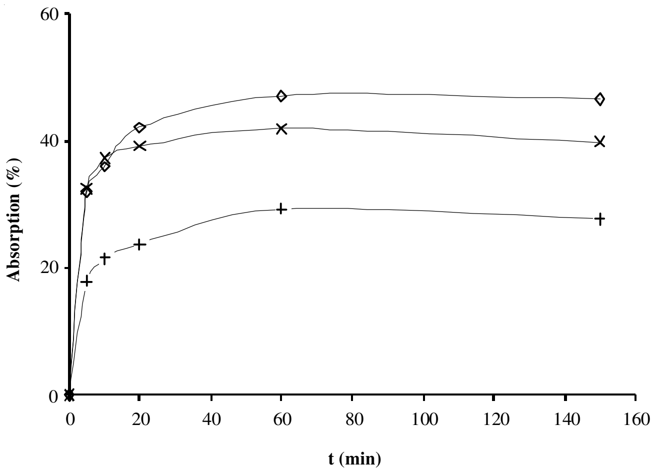

Fig. 1. Effect of contact time on adsorption of Cu^{2+} (◊ 10 mg/L, × 50 mg/L, + 100 mg/L)

ion concentration was observed to be removed. As reported in many studies, a large part of the reaction was complete at the end of 1 h and equilibrium were reached[16,17] and in high adsorption rates were observed in the first 5-10 min of the reaction[18,19].

Effect of pH: In order to investigate the effect of pH on biosorption the metal concentration in the working solution has been adjusted to 150 mg/L, 1 g of *Ulva lactuca* has been selected as the adsorbent and the initial pH has been adjusted to be between 2 and 6. During the initial studies, the pH of the solutions were adjusted to be in the range of 2-6 prior to the addition of *Ulva lactuca*. As seen in Fig. 2, the adsorption of Cu^{2+} is dependent on pH. The adsorption of Cu^{2+} increased with increasing pH, however, it has begun to slightly decrease at pH above 5.5. It has been reported in a conducted study that the amount of carboxylic acid in the cellular structure of *Ulva lactuca* and the pH of the medium were effective on the metal binding capacity[20]. Since as indicated by the conducted experiments and many reported studies the maximum adsorption for copper occurs at pH 5 and around that pH for different biosorbents, the initial pH has been taken to be 5 in the remaining parts of the study[21].

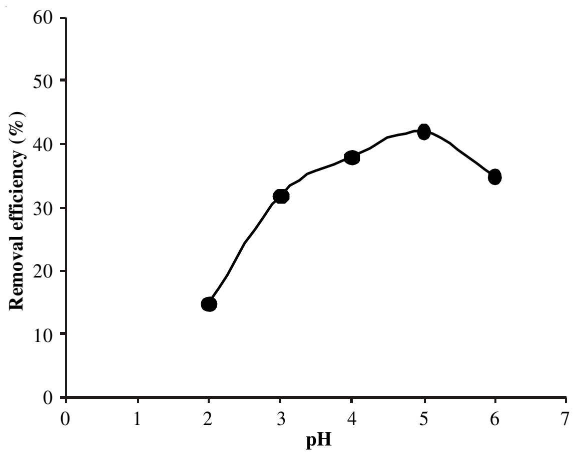

Fig.2. Effect of pH on adsorption of Cu^{2+}

Metal adsorption isotherms: The most highly correlated isotherms were determined to be the Langmuir and the

Freundlich isotherms when the sorption data were applied onto the isotherms and their correlation coefficients were determined as 99 and 97 %, respectively (Figs. 3 and 4).

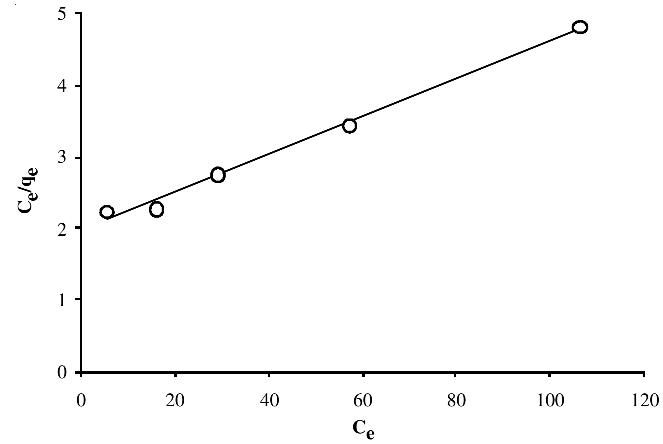

Fig. 3. Langmuir isotherm

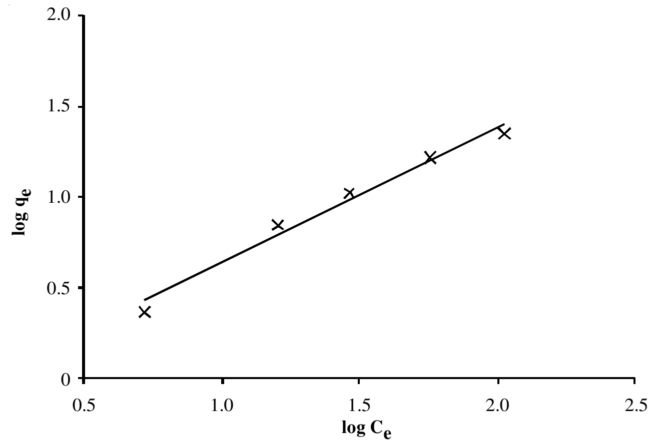

Fig. 4. Freundlich isotherm

The Q_m values in copper adsorption studies conducted by different biosorbents were compared in Table-2. The maximum metal adsorption capacity was calculated to be 38 mg/g from the Langmuir isotherm.

TABLE-2
COMPARISON OF THE Cu^{2+} ADSORPTION CAPACITIES OF VARIOUS BIOSORBENTS

Biosorbent	pH	Eqn. time (min)	Q_m (mg/g)
Fucus cerratus[22]	5.5	350	101
Bacillus sp.[21]	4.7	10	244
Rose waste[19]	5.0	20	55.79
Fucus vesiculosus[16]	5.5	60	23.4
Penicillium s.[23]	5.0	60	112.3
Fucus vesiculosus[24]	5.5	60	23.4
Ulva lactuca (this study)	5.0	60	38

Adsorption kinetics: The pseudo-first order (eqn. 3) and the pseudo-second order (eqn. 4) rate models have been applied to the experimental data in order to determine the adsorption rates at varying initial copper concentrations and they are displayed in Figs. 5 and Fig. 6.

Although the pseudo-first order rate model (Fig. 5) has low correlation values, the pseudo-second order rate model

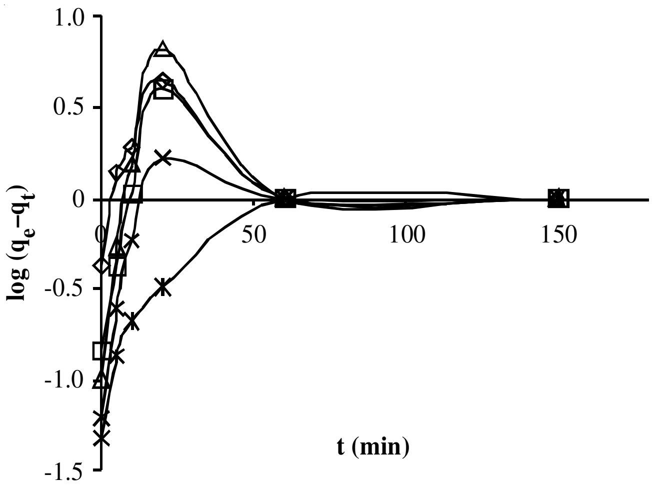

Fig. 5. Pseudo-first order plots (◊ 10 mg/L, □ 30 mg/L, × 50 mg/L, Δ 90 mg/L, O 150 mg/L)

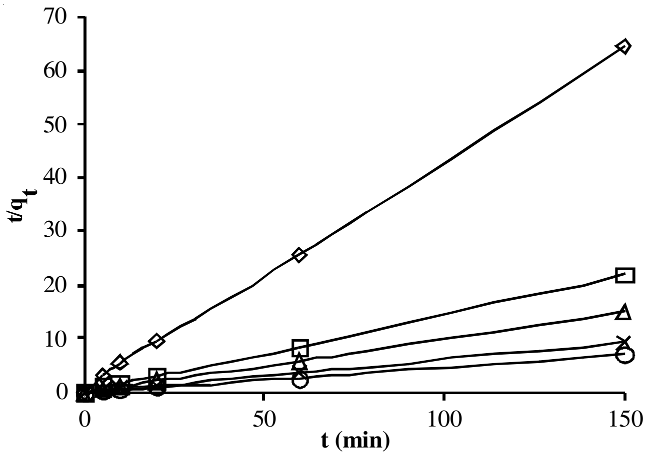

Fig. 6. Pseudo-second order plots (◊ 10 mg/L, □ 30 mg/L, × 50 mg/l, Δ 90 mg/L, O 150 mg/L)

(Fig. 6) has been highly correlated with approximately the same value of R^2: 0.95 for each concentration.

Conclusion

The adsorption studies indicated that untreated *Ulva lactuca* is a suitable biosorbent that could be used effectively in the removal of Cu^{2+} in aqueous solutions. The capacity of the biosorbent is dependent on pH and the contact time. The FT-IR analysis was showed that play a role effectively the functional groups in the structure of the biosorbent during adsorption.

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