REMOVAL OF CU^{2+} IONS FROM AQUEOUS SOLUTIONS USING *NANNOCHLOROPSIS OCULATA* BIOMASS

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Abstract. The aim of this study was to investigate the capacity of Nannochloropsis oculata biomass for Cu^{2+} ions removal from aqueous solutions. The initial concentrations of Cu^{2+} ions used to determine the maximum amount of Cu^{2+} ions adsorbed onto Nannochloropsis oculata biomass varied from 10 mg/L to 50 mg/L. The experimental data were analysed using Langmuir, Freundlich, and Dubinin-Radushkevisch isotherm models. The correlation regression coefficients show that the biosorption process can be well defined by the Langmuir equation. From the Dubinin-Radushkevich isotherm the mean free energy was calculated to be 10 kJ/mol, which indicates that Cu^{2+} ions biosorption is characterized by a chemical process.

Keywords: biosorption, Cu^{2+}, equilibrium, isotherm models, Nannochloropsis oculata

INTRODUCTION

Many industries such as mining and smelting of minerals and metals, surface finishing industry, fertilizer and pesticide industry, electrical and electroplating industries, discharge heavy metal effluents into the environment (Ahmady-Asbchin and Mohammadi, 2011; Al-Homaidan et al., 2014; Yilmaz et al., 2010). Thus, heavy metal pollution has emerged as a major concern threatening human health, natural resources and the ecosystems (Al-Homaidan et al., 2014).

Copper has been one of the most widely used metals for centuries and its presence in the environment causes serious toxicological concerns (Yilmaz et al., 2010).

Several physico-chemical methods have been developed for heavy metals removal from contaminated water, but these techniques present many disadvantages. Therefore, cost effective technologies or sorbents for treatment of metal contaminated waste streams are needed. (Ahmady-Asbchin and Mohammadi, 2011; Al-Homaidan et al., 2014).

Biosorption is an innovative technology that uses inexpensive dry biomass such as algae to extract the heavy metals. It is a promising alternative method to treat industrial effluents, mainly because it is available in large quantities, it is largely cultivated worldwide, and its processing is relatively cheap and has a high metal binding capacity (Ahmady-Asbchin and Mohammadi, 2011, Al-Homaidan et al., 2014; Horváthová et al., 2009; Ghoneim et al., 2014).

The main objective of the present study was to investigate the possible use of *Nannochloropsis oculata* biomass, a marine microalgae, as an alternative adsorbent for the removal of Cu^{2+} ions from aqueous solution.

MATERIALS AND METHODS

A stock solution of 100 ppm copper solution was prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ in deionized distilled water. Various concentrations of test solutions were prepared by appropriate dilution of the stock solution.

The biosorption experiments were performed in batch conditions, using 0.5 g *Nannochloropsis oculata* biomass as powder contacted with copper solutions (100 mL) at different initial concentrations (10 - 50 mg/L) at room temperature. The stirring rate was maintained at 500 rpm using a magnetic stirrer for 300 min. The adsorbate was then decanted and separated from the adsorbent after centrifugation (4500 rpm, for 20 min) followed by filtration using 0.45 µm membrane filters and mineralization with HNO_3. The concentration of copper in solution was determined using an inductively coupled plasma mass spectrometer, Perkin Elmer Elan DRC II.

The amount of Cu^{2+} ions adsorbed per unit mass of biomass was calculated using Eq.(1), while removal efficiency was calculated using Eq.(2).

$$q_e = \frac{(C_0 - C_e)}{m} \cdot \frac{V}{1000} \quad (1)$$

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

Where C_0 - initial Cu^{2+} ions concentration in solution (mg/L)

C_e - equilibrium metal ion concentration in solution (mg/L)

q_e - amount of Cu^{2+} ions adsorbed onto the biomass (mg/g)

V - volume of the medium (mL)

m - amount of the biomass (g)

E - removal efficiency (%) (Ghoneim et al., 2014)

RESULTS AND DISCUSSIONS

Effect of the initial concentration. The experiments were carried out using a fixed *Nannochloropsis oculata* biomass (0.5 g) and stirring rate (500 rpm) but varying the initial zinc concentration (10 - 50 mg/L). The obtained results for the biosorption of Cu^{2+} ions by *Nannochloropsis oculata* biomass starting from different initial concentrations are presented in Fig.1.

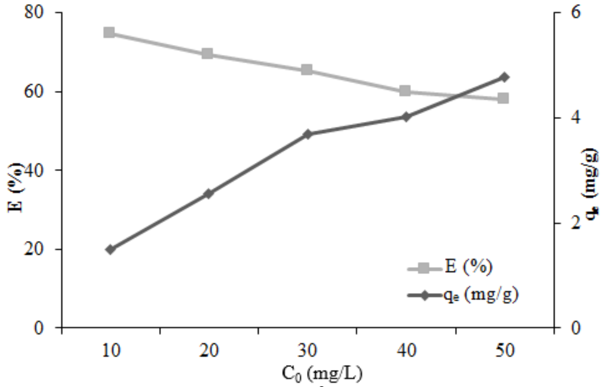


Fig. 1. The removal efficiency and amount of Cu^{2+} ions adsorbed onto *Nannochloropsis oculata* biomass at different concentrations

As it can be seen the amount of Cu^{2+} ions adsorbed onto the biomass at 10 mg/L was 1.5 mg/g (75% removal efficiency) and 4.8 mg/g (56% removal efficiency) at 50 mg/L. In the studied range of concentration, the removal efficiency of Cu^{2+} ions adsorbed slowly decreases as the initial concentration increases.

Isotherm models

The equilibrium data were analysed using Langmuir, Freundlich and Dubinin-Radushkevisch isotherm models.

The Langmuir isotherm equation (Langmuir, 1916), valid for monolayer adsorption onto specific homogenous sites is given below:

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \quad (3)$$

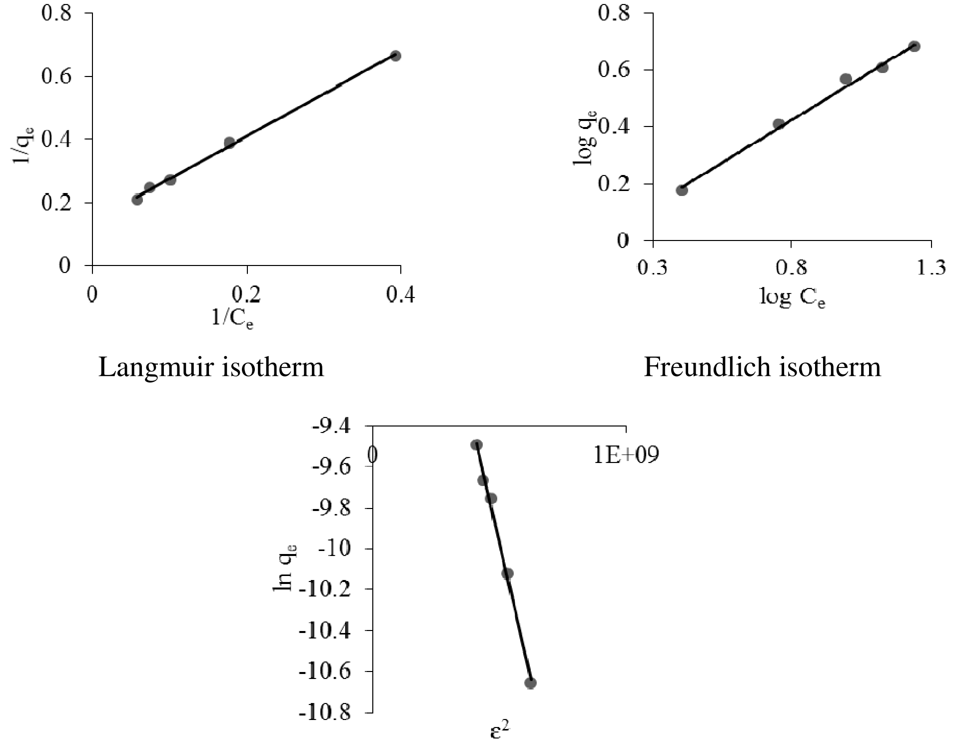
Where K_L - Langmuir constant (L/mg)

q_{max} - maximum uptake capacity (mg/g)

Also, Langmuir isotherm may be expressed by the separation factor R_L:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The calculated R_L values at different initial concentration (10 - 50 mg/L) are ranging between 0.16 - 0.49 indicating that the equilibrium biosorption was favourable, R_L value is between 0 and 1, (Ghoneim *et al.*, 2014). Figure 2 shows the Langmuir plots for biosorption of Cu^{2+} onto *Nannochloropsis oculata* at different concentrations. Isotherm parameters q_{max} and K_L obtained from the slope and intercept of the plot $1/q_e$ vs. $1/C_e$ are presented in Table 1.



Dubinin-Radushkevich isotherm

Fig. 2. Isotherm models for biosorption of Cu^{2+} ions onto *Nannochloropsis oculata* biomass

Table 1

Isotherm constants for biosorption of Cu^{2+} ions *Nannochloropsis oculata* biomass

Langmuir			Freundlich			Dubinin-Radushkevich		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F ($mg^{(1-1/n)}$ $L^{1/n}$ /g)	R^2	β (mol^2/ kJ^2)	E (kJ/mol)	R^2
7.15	0.10	0.9977	1.66	0.87	0.9919	$5 \cdot 10^{-9}$	10	0.9951

Freundlich isotherm (Freundlich, 1906) is used to describe the adsorption characteristics for the heterogeneous surface and it can be expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

Where K_F - Freundlich constant that indicate the capacity of the biosorption

n - Freundlich constant that indicate the intensity of the biosorption

$1/n$ - function of the strength of adsorption (Ghoneim et al., 2014).

From the data presented in Tab. 2, the value of n is 1.66 indicating that the biosorption of Cu^{2+} ions onto *Nannochloropsis oculata* is favourable (n value is between 1 and 10). Isotherm constant K_F, n and correlation coefficients were obtained from the slope and the intercept of the linear plot $\log q_e$ vs. $\log C_e$ at different concentrations (Fig. 2b).

Dubinin-Radushkevich isotherm (Dubinin, 1960) it is applied to express the adsorption process occurred onto both homogeneous and heterogeneous surfaces (Chen, 2015). The linear form is given below:

$$\ln q_e = \ln q_{max} - \beta \varepsilon^2 \tag{6}$$

Where β - Dubinin Radushkevich model constant (mol^2/kJ^2) (Sarı and Tuzen, 2008).

ε is equal to:

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \tag{7}$$

Where R - gas constant (8.314 J mol/K)

T - absolute temperature (K) (Sarı and Tuzen, 2008).

Free energy E_L per molecule, Eq.(8), of adsorbate, which helps to distinguish between the physical and chemical biosorption of metal ions is given below (Sarı and Tuzen, 2008):

$$E_L = \frac{1}{\sqrt{-2\beta}} \tag{8}$$

The isotherm constants q_m and β were obtained from the intercept and the slope of the plot $\ln q_e$ vs. ε^2. The mean free energy was 10 kJ/ mol (Tab. 2) indicating a chemical process (E_L value is between 8 and 16 kJ/mol).

CONCLUSIONS

Nannochloropsis oculata biomass, a marine microalga, was used as a biosorbent for the removal of Cu^{2+} ions from aqueous solution in batch mode.

The obtained values showed a classic behaviour: as the initial concentration increased, the amount of Cu^{2+} ions adsorbed onto the biomass increased, while removal efficiency decreased.

Experimental data fitted well on the considered isotherm models. Langmuir isotherm model had the highest regression value, suggesting a monolayer adsorption onto specific homogenous sites and a favourable biosorption of the considered heavy metal. Also the parameter predicted from Freundlich isotherm model indicate a favourable biosorption of Cu^{2+} ions onto *Nannochloropsis oculata* biomass. The Dubinin-Radushkevich isotherm model indicates that Cu^{2+} ions biosorption is characterized by a chemical process.

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