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REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTION BY BIOSORPTION ON MARINE ALGAE BIOMASS

BY

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Abstract. In this study, the marine algae biomass was used as biosorbent for the removal of Cu(II) ions from aqueous solution. The biosorption process was studied in batch systems at room temperature (19°C) as a function of initial Cu(II) concentration and contact time. The experimental results were analyzed using Langmuir and Freundlich models for isotherm modeling, and pseudo-first order and pseudo-second order models, for kinetics modeling. The Langmuir model best describe the biosorption isotherm of Cu(II) ions onto marine algae biomass, and the maximum biosorption capacity calculated in this case is 64.4445 mg·g⁻¹. The kinetics data are well fitted by pseudo-second model, which means that in the biosorption mechanism the rate limiting step is the chemical interaction between metal ions from aqueous solution and superficial functional groups of biomass. The results included in this study indicate that the marine algae biomass can be considered a viable biosorbent for the removal of Cu(II) ions from aqueous solution.

Key words: Cu(II) ions; marine algae biomass; biosorption; isotherm; kinetics.

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1. Introduction

The pollution of water with metal ions discharged from industrial activities has become in the last years, an important problem in many regions of the world, mainly because the metal ions have a toxic effect on most life forms, are not biodegradable and tend to accumulate in the environment. Therefore, the industrial effluents that contain metal ions must be treated in order to remove such contaminants, and gain secure sources of water that can be recycled (Wang & Chen, 2009).

In order to treat aqueous effluents that contains important concentrations of metal ions, numerous treatment methods can be used (such as chemical precipitation, extraction, ion exchange, reverse osmosis, filtration, membrane related processes, electrochemical techniques, etc.) (Dabrowski *et al.*, 2004; Romera *et al.*, 2007; Abdolali *et al.*, 2014; Luo *et al.*, 2011), and many of these are employed at industrial scale. Unfortunately, these treatment methods are not effective in low metal ions concentration range, can be sometimes very expensive due to the high chemical reagents and energy requirements, and generate secondary sludge that generate some problems related to its disposal (Sud *et al.*, 2008).

In comparison with these, the biosorption is a fast and versatile method that can be used for the removal of metal ions from aqueous effluents with high efficiency and relatively low cost. All these advantages are determined by the ease with which various natural materials or certain waste products from industrial and agricultural activities, can bind metal ions from aqueous solutions. In addition, when such materials are available in large quantities and require only few step of preparation, beside technological performances, the economic viability of biosorption process is also high.

The marine algae biomass is one example of such low-cost biosorbent that can be used for the removal of heavy metal ions from aqueous media. Many studies from literature have shown that marine algae biomass have an excellent retention capacity for various metal ions (Lodeiro *et al.*, 2006; Chen *et al.*, 2011; Lupea *et al.*, 2012), due to the variety of functional groups from polysaccharides, proteins or lipids from cell walls surface (Donmez *et al.*, 1999; Hamdy, 2000). All these characteristics make that in the biosorption process, the marine algae biomass to act as a chemical substrate of biologic origin, which can retain metal ions on their surface by specific interactions with superficial functional groups, such as ion exchange, electrostatic, complexation, or even micro-precipitation (Mack *et al.*, 2007; Pahlavanzadeh *et al.*, 2010).

In this study, the marine algae biomass was used as low-cost biosorbent for the removal of Cu(II) ions from aqueous solution. The biosorption process was studied in batch systems at room temperature (19°C) and have followed the influence of initial Cu(II) ions concentration and contact time on the biosorption efficiency. The equilibrium and kinetics experimental results have been

analyzed using two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order), and the characteristic parameters of each model has been calculated. The data presented in this study indicate that marine algae biomass can be used as a low-cost biosorbent for the removal of Cu(II) ions from aqueous solution, and this method can become a viable option for the treatment of wastewater contaminated with such metal ions.

2. Experimental

2.1. Materials

All chemical reagents used in this study were of analytical grade and were used without purification. In all experiments distilled water, obtained from a commercial distillation system, was used for the preparation and dilution of solutions. Stock solution of copper(II) ($660 \text{ mg Cu(II)} \cdot \text{L}^{-1}$) was prepared by dissolving copper sulfate salt in distilled water. The stock solution was used then to obtain working solutions, by dilution. Fresh dilutions were prepared for each experiment. The pH of each working solution was adjusted to 5.0 with $10^{-3} \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ solution, before mixing the biomass.

The marine algae biomass was obtained from *Ulva lactuca* marine green algae collected from Romanian Coast of Black Sea. After several washes with sea and distilled water to remove impurities, the marine algae were dried in air at 70°C for 24 h. The obtained biomass was crushed and sieved until the grain-size of particles was between 1.0 – 1.5 mm, and then stored in desiccators for further use.

2.2. Methods

The biosorption experiments were performed in batch systems, at room temperature (19°C), mixing samples of 0.2 g of marine algae biomass with 25 mL of Cu(II) solution of known concentration at pH of 5.0, in 150 mL conical flasks. This values of initial solution pH as well as the biosorbent dose ($8.0 \text{ g} \cdot \text{L}^{-1}$) were established previously (Bulgariu & Bulgariu, 2012) as optimum for metal ions biosorption on marine algae biomass. A series of solutions with initial Cu(II) concentration between 13 and $210 \text{ mg} \cdot \text{L}^{-1}$ were added to 0.2 g of biomass and intermittently shaken for 24 h. For the kinetics experiments, the same amount of biosorbent (0.2 g) was mixed with 25 mL of $79 \text{ mg Cu(II)} \cdot \text{L}^{-1}$ solution at various time intervals between 5 and 180 min. After biosorption procedure was complete, the solid and liquid phases were separated through filtration, and the Cu(II) concentration in filtrate was analyzed spectrophotometrically with rubeanic acid (Digital Spectrophotometer S104 D, 1 cm glass cell, $\lambda = 390 \text{ nm}$, against blank solution) (Dean, 1995). The biosorption capacity of marine algae biomass for Cu(II) ions (q , [$\text{mg} \cdot \text{g}^{-1}$]) and the Cu(II) removal percent (R , [%]) were calculated from experimental results, using the following equations:

$$q = \frac{c_0 - c}{m} \cdot V \quad (1)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where: c_0 and c are the concentration of Cu(II) ions in the initial solution and at the equilibrium after the biosorption experiments, [$\text{mg}\cdot\text{L}^{-1}$]; V – the volume of solution, [L]; m – the amount of marine algae biomass, [g].

3. Results and Discussions

3.1. Effect of Initial Cu(II) Concentration and Equilibrium Modeling

The effect of initial Cu(II) concentration on the biosorption efficiency on marine algae biomass is illustrated in Fig. 1. The increase of initial Cu(II) ions concentration from 13 to 210 $\text{mg}\cdot\text{L}^{-1}$ determined a increase of biosorption capacity (q , [$\text{mg}\cdot\text{g}^{-1}$]) from 1.12 to 20.28 $\text{mg}\cdot\text{g}^{-1}$, while the removal percent (R , [%]) slowly decrease (from 83.64 to 78.43 %).

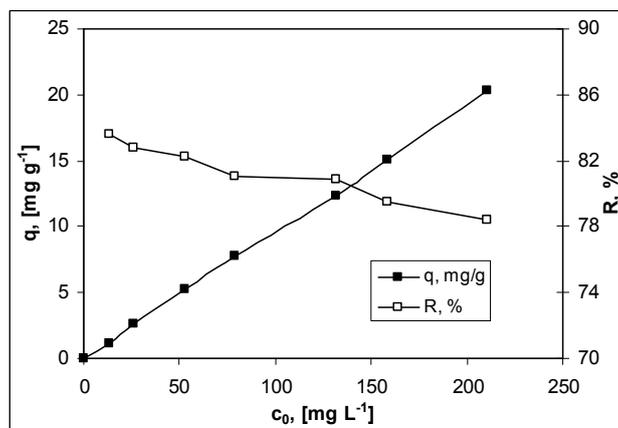


Fig. 1 – Effect of initial Cu(II) concentration on removal efficiency onto marine algae biomass (pH = 5.0; 8.0 g biosorbent $\cdot\text{L}^{-1}$; 24 h of contact time; 19°C).

As can be observed from Fig. 1, the highest retention of Cu(II) correspond to highest initial metal ions concentration, because under these conditions the ratio between the number of Cu(II) ions and the number of available biosorption sites from marine algae biomass surface is higher (Krishnan & Anirudhan, 2003). However, the variation of removal percent values also presented in Fig. 1, indicate that at higher concentration of Cu(II) ions in aqueous solution, the available biosorption sites from biomass surface

are already occupied, and this make that the diffusion of Cu(II) ions to the unreacted functional groups be hampered.

The isotherm obtained in case of Cu(II) ions biosorption onto marine algae biomass was analyzed using two isotherm models, namely Langmuir and Freundlich, whose mathematical equations are presented in Table 1.

Table 1
Mathematical Equations of Langmuir and Freundlich Isotherm Models
(Chong & Volesky, 1995; Rangabhashiyam *et al.*, 2014)

Model	Mathematical Equation	Notations
Langmuir	$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c}$	q – biosorption capacity of marine algae biomass for Cu(II) at equilibrium; q_{\max} – maximum biosorption capacity; K_L – Langmuir constant
Freundlich	$\lg q = \lg K_F + \frac{1}{n} \lg c$	K_F – Freundlich constant; n – heterogeneity factor.

These two models have been choice for the modeling of experimental data due to their usefulness in the description of biosorption mechanism. Thus, if the Langmuir model assumes that the biosorption of metal ions occurs on homogeneous biosorption sites until complete monolayer coverage is formed at the biomass surface, the Freundlich model consider that the biosorption take place on heterogeneous surface and is not restricted to the formation of monolayer (Chong & Volesky, 1995; Rangabhashiyam *et al.*, 2014).

The isotherm parameters for each model were calculated from the slopes and intercepts of their linear representations (Fig. 2), and the obtained values are summarized in Table 2.

The values of correlation coefficients (R^2) show that the biosorption data obtained in case of Cu(II) ions onto marine algae biomass are better described by Langmuir model than Freundlich model. This indicate that the surface of marine algae biomass is up of homogeneous biosorption patches and demonstrate the formation of monolayer coverage of Cu(II) ions on the outer surface of biomass. The maximum biosorption capacity ($q_{\max} = 69.4445 \text{ mg}\cdot\text{g}^{-1}$) is higher than the experimental value ($20.28 \text{ mg}\cdot\text{g}^{-1}$), and this indicate that even at highest initial Cu(II) concentration, on marine algae biomass surface are still un-occupied available biosorption sites, which can be involved in biosorption process.

Table 2
Isotherm Parameters Calculated for the Biosorption of Cu(II) on Marine Algae Biomass

Isotherm Model	Parameter	Obtained Value
Langmuir	R^2	0.9984
	q_{\max} , [mg·g ⁻¹]	69.4445
	K_L , [L·mg]	0.0087
Freundlich	R^2	0.9516
	n	1.0163
	K_F , [(mg·g ⁻¹) (L·mg ⁻¹) ^{1/n}]	0.4549

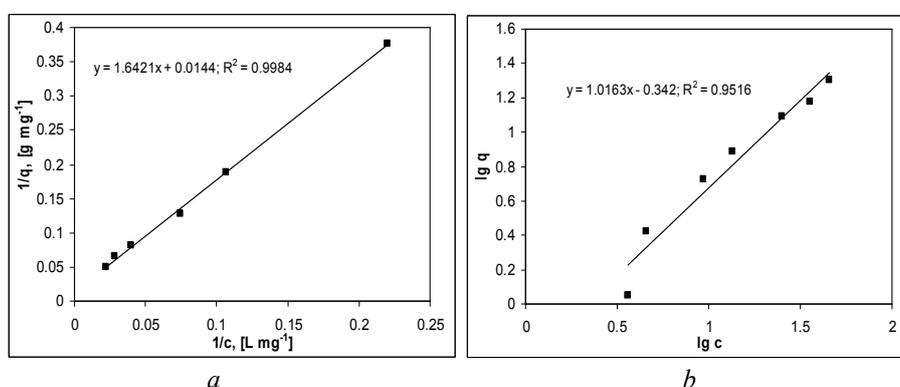


Fig. 2 – Linear representation of Langmuir (a) and Freundlich (b) isotherm models for the biosorption of Cu(II) ions onto marine algae biomass (pH = 5.0; 8.0 g biomass·L⁻¹; 24 h of contact time; 19°C).

Also, the relatively high value of Langmuir constant (K_L) suggest that between Cu(II) ions from aqueous solution and superficial functional groups of biomass occurs strong interaction, and these represent the driving force of biosorption process.

3.2. Effect of Contact Time and Kinetics Modeling

The influence of contact time on the biosorption efficiency of Cu(II) ions from aqueous solution onto marine algae biomass is presented in Fig. 3.

It can be observed that for an initial Cu(II) concentration of 79.10 mg·L⁻¹, the biosorption efficiency of Cu(II) ions significantly increase within first 30 min, when more than 80% of metal ions are retained. With the gradual occupation of binding sites, the Cu(II) uptake process requires the penetration of the inner active sites, which make that the biosorption process to become slower. Therefore, in case of Cu(II) ions biosorption onto marine algae biomass, in

mentioned experimental conditions, the time necessary to attain the equilibrium is at least 60 min.

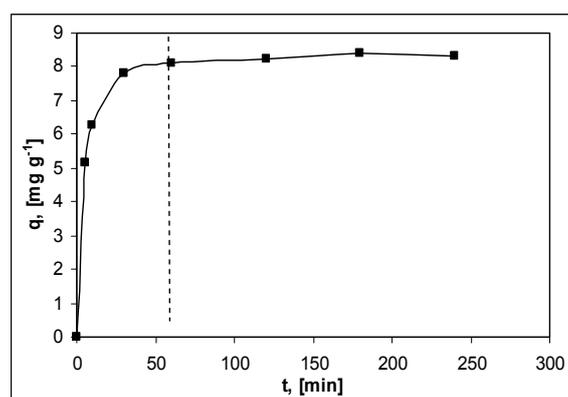


Fig. 3 – Effect of contact time for Cu(II) biosorption onto marine algae biomass (pH = 5.0; $c_0 = 79.10 \text{ mg}\cdot\text{L}^{-1}$; $8.0 \text{ g biosorbent}\cdot\text{L}^{-1}$; 19°C).

The very fast biosorption of Cu(II) ions on algae biomass shows that the functional groups of this material are predominantly located at the surface and have a high availability degree to interact with metal ions from aqueous solution.

In order to analyze the kinetics of Cu(II) biosorption onto marine algae biomass, two kinetics models, namely pseudo-first order and pseudo-second order models, were used to test the experimental data. The mathematical equations of these two kinetics models are given by the following relations (Gerente *et al.*, 2007):

$$\text{a) pseudo-first order model: } \lg(q_e - q_t) = \lg q_e - k_1 \cdot t \quad (3)$$

$$\text{b) pseudo-second order kinetic model: } \frac{1}{q_e} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (4)$$

where: q_e is the biosorption capacity at equilibrium, [$\text{mg}\cdot\text{g}^{-1}$]; q_t – biosorption capacity at time t , [$\text{mg}\cdot\text{g}^{-1}$]; k_1 – the rate constant of pseudo-first order kinetic model, [min^{-1}]; k_2 – the rate constant of pseudo-second order kinetic model, [$\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$].

The linear representations of the of the pseudo-first order and the pseudo-second order kinetics models for the biosorption of Cu(II) ions onto marine algae biomass are presented in Fig. 4, and the values of kinetics parameters calculated from the regression equations obtained in each case, are summarized in Table 3.

As can be observed from Fig. 4 and Table 3, the correlation coefficient (R^2) for the pseudo-first order kinetic equation is only 0.9096 and the equilibrium biosorption capacity (q_e , [$\text{mg}\cdot\text{g}^{-1}$]) calculated from eq. (3) has the

value of $2.2506 \text{ mg}\cdot\text{g}^{-1}$, which is much lower than those obtained experimentally ($8.3870 \text{ mg}\cdot\text{g}^{-1}$). Therefore, the pseudo-first order kinetics model is not suitable for providing a description of Cu(II) ions biosorption onto marine algae biomass.

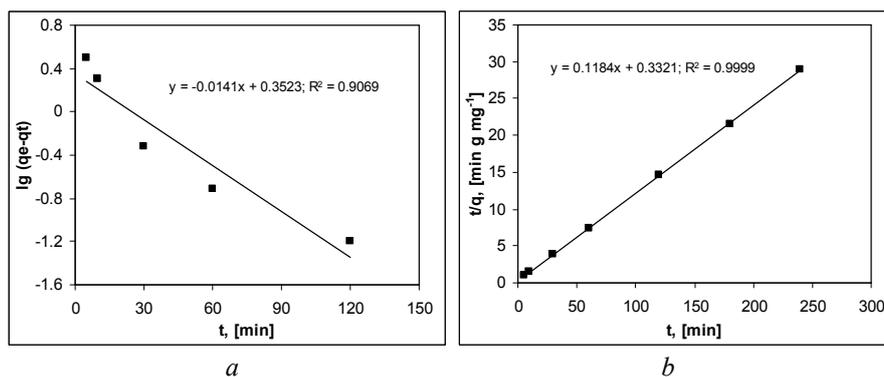


Fig. 4 – Linear representation of pseudo-first order (a) and pseudo-second order (b) kinetics models for the biosorption of Cu(II) ions onto marine algae biomass (pH = 5.0; $c_0 = 79.10 \text{ mg}\cdot\text{L}^{-1}$; $8.0 \text{ g biosorbent}\cdot\text{L}^{-1}$; 19°C).

Table 4

Kinetics Parameters Calculated for the Biosorption of Cu(II) on Marine Algae Biomass

Kinetics Model	Parameter	Obtained Value
Pseudo-first order	R^2	0.9096
	$q_e, [\text{mg}\cdot\text{g}^{-1}]$	2.2506
	$k_1, [\text{min}^{-1}]$	0.0141
Pseudo-second order	R^2	0.9999
	$q_e, [\text{mg}\cdot\text{g}^{-1}]$	8.4459
	$k_2, [\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}]$	0.0422

On the other hand in case of pseudo-second order kinetics model, the high value of correlation coefficient ($R^2 = 0.9999$) and the close value of q_e calculated from eq. (4) with the one obtained experimentally (Table 3), clearly indicate that this model is adequate in describing the biosorption kinetics of Cu(II) ions onto marine algae biomass.

The pseudo-second order kinetic model assume that in the uptake process of Cu(II) ions from aqueous solution, the rate limiting step is chemical biosorption, which involves the sharing of exchange of electrons between biosorbent and metal ions (Ho *et al.*, 1996). The good correspondence of the experimental data with this model suggest that the chemical interaction between Cu(II) ions and superficial functional groups of marine algae biomass is the rate controlling step of this process, and in consequence the biosorption takes place in gradually, until a complete monolayer coverage is formed.

4. Conclusions

In this study was examined the removal of Cu(II) ions from aqueous solution onto marine algae biomass. The biosorption process was studied in batch systems at room temperature (19°C) as a function of initial Cu(II) concentration and contact time. The Langmuir and Freundlich isotherm models were used to provide the mathematical description of the experimental data of biosorption process. The results indicate that the equilibrium data are very well fitted by Langmuir model, and maximum biosorption capacity calculated in this case is 64.4445 mg·g⁻¹. The biosorption of Cu(II) ions onto marine algae biomass followed the pseudo-second order kinetic model, indicating that the rate controlling step of this process is the chemical interaction between Cu(II) ions and superficial functional groups of biomass. The results included in this study indicate that marine algae biomass can be considered a viable low-cost biosorbent for the removal of Cu(II) ions from aqueous solution.

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REFERENCES

- Abdolali A., Guo W.S., Ngo H.H., Chen S.S., Nguyen N.C., Tung K.L., *Typical Lignin-Cellulosic Wastes and by-Products for Biosorption Process in Water and Wastewater Treatment: A Critical Review*. *Biores. Technol.*, **160**, 57–66 (2014).
- Bulgariu D., Bulgariu L., *Equilibrium and Kinetics Studies of Heavy Metal Ions Biosorption on Green Algae Waste Biomass*. *Biores. Technol.*, **103**, 489–493 (2012).
- Chen Y., Dong R., Peng G., Yi Z., Huo S., Liu Y., Pang C., *Cultivation of Chlorella sp. in Anaerobic Effluent for Biomass Production*. *Environ. Eng. Manag. J.*, **10**, 909–912 (2011).
- Chong K.H., Volesky B., *Description of 2-Metal Biosorption Equilibria by Langmuir-Type Models*. *Biotech. Bioeng.*, **47**, 451–460 (1995).
- Dabrowski A., Hubicki Z., Podkoscielny P., Robens E., *Selective Removal of the Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method*. *Chemosphere*, **56**, 91–106 (2004).
- Dean J.A., *Analytical Chemistry Handbook*, New York: McGraw-Hill, Inc. (1995).
- Donmez G., Aksu Z., Ozturk A., Kutsal T., *A Comparative Study on Heavy Metal Biosorption Characteristics of Some Algae*. *Process Biochem.*, **34**, 885–892, (1999).
- Gerente C., Lee V.K.C., Lee P., McKay G., *Application of Chitosan for the Removal of Metals from Wastewaters by Adsorption - Mechanisms and Models Review*. *Critical Rev. Environ. Sci. Technol.*, **37**(1), 41–127, (2007).
- Hamdy A.A., *Biosorption of Heavy Metals by Marine Algae*. *Curr. Microbiol.*, **41**, 232–238 (2000).
- Ho Y.S., John Wase D.A., Forster C.F., *Kinetic Studies of Competitive Adsorption by Sphagnum Moss Peat*. *Environ. Technol.*, **17**, 71–77 (1996).

- Krishnan K.A., Anirudhan T.S., *Removal of Cadmium(II) from Aqueous Solutions by Stream-Activated Sulphurised Carbon Prepared from Sugar-Cane Bagasse Pith: Kinetics and Equilibrium Studies*. Water SA, **29**, 147–156 (2003).
- Lodeiro P., Barriada J.L., Herrero R., Sastre de Vicente M.E., *The Marine Macroalga Cystoseira Baccata as Biosorbent for Cadmium(II) and Lead(II) Removal: Kinetic and Equilibrium Studies*. Environ. Poll., **142**, 264–273 (2006).
- Luo X., Deng Z., Lin X., Zhang C., *Fixed-bed Column Study for Cu²⁺ Removal from Solution Using Expanding Rice Husk*. J. Hazard. Mater., **187**, 182–189 (2011).
- Lupea M., Bulgariu L., Macoveanu M., *Biosorption of Cd(II) from Aqueous Solution on Marine Green Algae Biomass*. Environ. Eng. Manag. J., **11**, 3, 607–615 (2012).
- Mack C., Wilhelmi B., Duncan J.R., Burgess J.E., *Biosorption of Precious Metals*. Biotechnol. Adv., **25**, 264–271 (2007).
- Pahlavanzadeh H., Keshtkar A.R., Safdari J., Abadi Z., *Biosorption of Nickel(II) from Aqueous Solution by Brown Algae: Equilibrium, Dynamic and Thermodynamic Studies*. J. Hazard. Mater., **175**, 304–310 (2010).
- Rangabhashiyam S., Anu N., Nandagopal Giri M.S., Selvaraju N., *Relevance of Isotherm Models in Biosorption of Pollutants by Agricultural by-Products*. J. Environ. Chem. Eng., **2**, 1, 398–414 (2014).
- Romera E., Gonzalez F., Ballester A., Blazquez M.L., Munoz J.A., *Comparative Study of Biosorption of Heavy Metals Using Different Types of Algae*. Bioresour. Technol., **98**, 3344–3353 (2007).
- Sud D., Mahajan G., Kaur M.P., *Agricultural Waste Material as Potential Adsorbent for Sequestering Heavy Metal Ions from Aqueous Solutions – A Review*. Biores. Technol., **99**, 6017–6027 (2008).
- Wang J., Chen C., *Biosorbents for Heavy Metals Removal and their Future*. Biotechnol. Adv., **27**, 195–226 (2009).

ÎNDEPĂRTAREA IONILOR DE Cu(II) DIN SOLUȚII APOASE PRIN BIOSORBȚIE PE BIOMASĂ DE ALGE MARINE

(Rezumat)

În acest studiu, biomasa de alge marine a fost utilizată ca biosorbent pentru îndepărtarea ionilor de Cu(II) din soluții apoase. Procesul de biosorbție a fost studiat în sistem discontinuu la temperatura camerei (19°C) în funcție de concentrația inițială a Cu(II) și de timpul de contact. Rezultatele experimentale au fost analizate utilizând modelele Langmuir și Freundlich pentru modelarea izotermelor, și modelele de ordin pseudo-unu și pseudo-doi, pentru modelarea cinetică. Modelul Langmuir descrie cel mai bine izoterma de biosorbție a ionilor de Cu(II) pe biomasa de alge marine, iar capacitatea maximă de biosorbție calculată în acest caz este de 64.4445 mg·g⁻¹. Datele cinetice sunt bine descrise de modelul de ordin pseudo-doi, ceea ce înseamnă că în mecanismul de biosorbție, etapa determinantă de viteză este interacția chimică dintre ionii metalici din soluția apoasă și grupările funcționale superficiale ale biomasei. Rezultatele incluse în acest studiu indică faptul că biomasa de alge marine poate fi considerată un biosorbent viabil pentru îndepărtarea ionilor de Cu(II) din soluții apoase.