BIOSORPTION POTENTIAL OF VARIOUS WASTE BIOMASSES FOR Cu(II) IONS REMOVAL FROM AQUEOUS SOLUTION

POTENȚIALUL BIOSORPTIV AL UNOR DEŞEURI DE BIOMASĂ PENTRU ÎNDEPĂRTAREA IONILOR DE Cu(II) DIN SOLUȚII APOASE

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Abstract. *In this study, was analyzed the biosorption potential of some waste biomasses in the removal process of Cu(II) ions from aqueous solution. Three types of biosorbents have been used in experiments, namely: marine algae waste, mustard waste and lignin. All these materials are resulted from different industrial activities, and their use for the metal ions removal from aqueous solution is in agreement with the principles of circular economy. The experimental results obtained for the influence of initial Cu(II) ions concentration and contact time on the removal efficiency from aqueous media were modelled using various isotherm and kinetics models. The parameters obtained from modelling have permitted the evaluation of biosorptive potential of these three types of waste biomasses in the removal processes of Cu(II) ions from aqueous solution.*

Key words: metal ions, waste biomass, biosorption, aqueous solution.

Rezumat. *In acest studiu a fost analizat potențialul biosorptiv al unor deşeuri de biomasă, pentru îndepărtarea ionilor de Cu(II) din soluții apoase. Trei tipuri de biosorbenți au fost utilizați pentru realizarea experimentelor, şi anume: deşeuri de mustar, deşeuri de alge marine şi lignină. Toate aceste materiale rezultă din diferite activități industriale, iar utilizarea lor pentru îndepărtarea ionilor metalici din soluții apoase este în concordanță cu principiile economiei circulare. Datele experimentale obținute în urma studiului influenței concentrației inițiale a ionilor de Cu(II) şi a timpului de contact asupra eficienței îndepărtării acestuia din medii apoase au fost modelate utilizând diferite modele cinetice şi ale izotermelor de biosorpție. Parametrii obținuți în urma modelării au permis evaluarea potențialului biosorptiv ale celor trei tipuri de deşeuri de biomase în procesele de îndepărtare a ionilor de Cu(II) din soluții apoase.*

Cuvinte cheie: ioni metalici, deşeuri de biomasă, biosorbție, soluții apoase.

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INTRODUCTION

Copper is a heavy metal with large industrial applications, such as electroplating, mining, alloys and conductors manufacturing, automobiles industry, pigments and painting, etc. But regardless of the industrial activity in which it originates, the directly discharge of the industrial effluents in the environment is prohibited by current legislation. This is because the copper is non-biodegradable and at high concentration is harmful for humans and other life forms (Barakat, 2011; Fu and Wang, 2011).

The retention of metal ions from aqueous solution on solid materials has begun to play an important role in the pollution control of industrial effluents, in special when these materials are inexpensive (Demirbas, 2008; Barakat, 2011). Thus, numerous studies from literature describe the utilization of various low-cost materials (such as peat, algae biomass, various agricultural residues, industrial by-products, etc.) (Gogate and Pandit, 2004; Demirbas, 2008) for the Cu(II) ions removal from aqueous media. The main advantages for the utilization of such materials in the metal ions biosorption are: (i) their very low cost and large availability, (ii) requires only few steps for the preparation and (iii) do not require complicated regeneration procedures (Demirbas, 2008). But, most of these low-cost materials have already other consecrated economic uses, which make that their eventual utilization as biosorbents to required rigorous economic and technological arguments. From this perspective, more appropriate could be the use of waste biomasses for the removal of metal ions from aqueous effluents. In this case beside that such utilization is in agreement with the principles of circular economy, can also be an ecological alternative for the environment protection.

In this study, the biosorption potential of some waste biomasses for Cu(II) ions removal from aqueous solution was examined in batch systems. The waste biomasses used for the experiments have been: marine algae biomass, mustard waste biomass and lignin, and these are derived from biofuels production, or pulp and paper manufacturing industry. The experimental data obtained from the influence of initial Cu(II) ions concentration and contact time on the biosorption efficiency on each type of biomass were modelled using two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order). The parameters calculated for each model have allowed the evaluation of biosorption potential of these three types of waste biomasses in the removal processes of Cu(II) ions from aqueous solution.

MATERIAL AND METHOD

The chemical reagent used for experiments were of analytical grade and were used without further purifications. The stock solution of Cu(II) ions (10^{-2} mol Cu(II)/L) was prepared from copper sulfate dissolving in distilled water. The working solutions were freshly prepared by dilution from the stock solution. 0.1 N HNO_3 solution was used for the adjusting of initial solution pH at desired value (6.0). The waste biomasses used as biosorbents in this study were obtained as follows: marine algae biomass and mustard waste biomass were prepared from marine algae biomass and mustard biomass after oil extraction in a Soxhlet extractor with n-hexane for 24 hour, while the lignin was obtained by precipitation, in acid media, from black liquor resulted from woodworking. All the biosorbents were dried in air at 50-55 °C, mortared and stored in desiccators for further use. The biosorption experiments were performed in batch systems, at room temperature (22 ± 2 °C), by mixing biosorbent samples (0.125 g) with 25 mL of Cu(II) ions solution of known concentration, in 100 mL conical flasks. The influence of initial Cu(II) ions concentration was studied in the concentration range between 12.41 and 257.54 mg/L and a contact time of 24 hours. In case of contact time, the same amount of biosorbent (0.125 g) was mixed with 25 mL of 51.51 mg Cu(II)/L solution for different times intervals (between 5 and 180 min). At the end of biosorption experiments, the phases were separated by filtration, and the Cu(II) concentration in solution was analyzed spectrophotometrically with rubeanic acid (Digital Spectrophotometer S104 D, 1 cm glass cell, λ = 390 nm, against blank solution). The biosorption capacity (q, mmol/g) and percents of removal (R,%) of each waste biomass for Cu(II) ions were calculated according with their definition.

The mathematical equation of the isotherm models (Langmuir and Freundlich) and kinetics models (pseudo-first order and pseudo-second order) used for the modeling of the experimental data were taken from the literature (Gerente *et al.*, 2007).

RESULTS AND DISCUSSIONS

Our previous studies (Bădescu *et al.*, 2015; Todorciuc *et al.*, 2015) have shown that the optimum initial solution pH for the Cu(II) biosorption on these waste materials was around 6.0. Even if in case of marine algae waste biomass and mustard waste biomass the initial pH established as optimum was 5.5, the final pH measured after biosorption was around 6.0. In order to evaluate the biosorption potential of these three waste biomass for Cu(II) ions, this value of pH was maintained, in all the experiments.

The effect of initial Cu(II) ions concentration on the biosorption performances of considered waste biomasses is illustrated in figure 1. As can be observed, the increase of Cu(II) ions concentration determined the increase of the biosorption capacities of each biosorbent, and follows the order: lignin > mustard waste > marine algae waste.

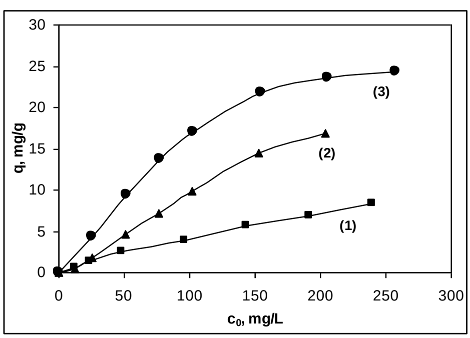
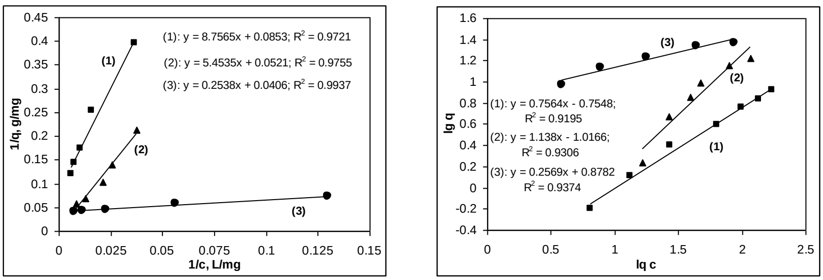


Fig. 1 Influence of initial Cu(II) ions concentration on the biosorption efficiency on (1) marine algae waste, (2) mustard waste and (3) lignin.

Such behavior is a consequence of the fact that the increase of initial Cu(II) ions concentration determine the increase of collision probability between metal ions and functional groups of biosorbents (Cruz *et al.*, 2004). On the other hand, the higher biosorption capacity of lignin for Cu(II) ions in comparison with marine algae waste and mustard waste, indicates that this biosorbent has a high number of functional groups, which are available for interactions with metal ions from aqueous solution.

In order to obtain a quantitative measure of the biosorption potential of these three biosorbents for Cu(II) ions, the experimental data were analyzed using Langmuir and Freundlich isotherm models. The linear representations of each isotherm model are presented in figure 2, and the calculated isotherm parameters are summarized in table 1.



(a) (b)

Fig. 2 Linear representations of Langmuir (a) and Freundlich (b) isotherm models for Cu(II) biosorption on (1) marine algae waste, (2) mustard waste and (3) lignin.

Table 1

Isotherm parameters for Cu(II) ions biosorption on the studied biosorbents

Isotherm model(*)		Marine algae waste	Mustard waste	Lignin
Langmuir	R^2	0.9721	0.9755	0.9937
	q_{max}, mg/g	11.7233	19.1938	24.6305
	K_L, g/L	0.0097	0.0095	0.1599
Freundlich	R^2	0.9195	0.9306	0.9374
	1/n	0.7564	1.1380	0.2569
	K_F, g/L	5.6859	0.0962	7.5544

On the basis of correlation coefficients (R^2) it can be noted that the Langmuir model has the higher applicability in the description of Cu(II) ions biosorption on the considered biosorbents. Therefore, the biosorption process takes place until to the formation of monolayer coverage on the biosorbent surface (Gerente *et al.*, 2007). Also, the maximum biosorption capacity (q_{max}, mg/g) increase in the order: marine algae waste < mustard waste < lignin, in agreement with the previous observations, which have suggest the higher biosorption potential of lignin in comparison with the other two biosorbents.

The second parameter, important in the evaluation of biosorption potential is the contact time. The experimental results obtained at the study of contact time effect on the biosorption efficiency of Cu(II) ions on considered biosorbents is presented in figure 3.

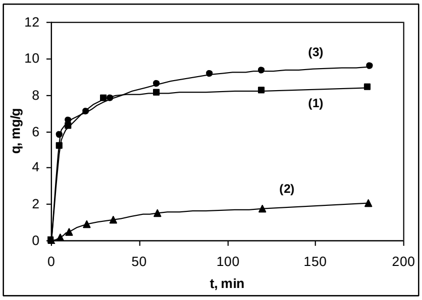
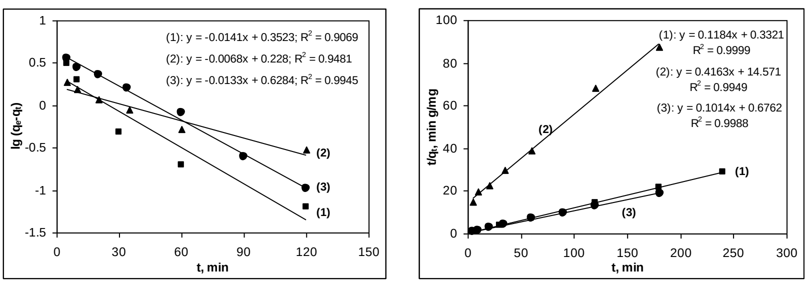


Fig. 3 Influence of contact time on the Cu(II) biosorption efficiency on (1) marine algae waste, (2) mustard waste and (3) lignin.

The experimental results from figure 3 indicates that the biosorption efficiency of Cu(II) ions on considered biosorbents increase with the contact time, and attains the maximum after 30 min in all cases. In this time interval the most efficient biosorbent is lignin (R > 83 %), followed by marine algae waste (R > 79 %) and mustard waste (R > 11 %).

The kinetics modelling of the experimental data illustrated in figure 3 was done using the pseudo-first order and the pseudo-second order kinetics models. The linear representations of these two models are illustrated in Fig. 4, and the calculated kinetics parameters are summarized in table 2.



(a) (b)

Fig. 4 Linear plots of pseudo-first order (a) and pseudo-second order (b) kinetics models, for Cu(II) biosorption on (1) marine algae waste, (2) mustard waste and (3) lignin.

Table 2

Kinetics parameters for Cu(II) ions biosorption on the studied biosorbents

Kinetics model		Marine algae waste	Mustard waste	Lignin
Pseudo-first order kinetics model	R^2	0.9069	0.9481	0.9945
	q_e, mg/g	2.2506	1.6904	4.2501
	k_1, 1/min	0.0061	0.0029	0.0057
Pseudo-second order kinetics model	R^2	0.9999	0.9949	0.9988
	q_e, mg/g	8.9459	2.4021	9.8621
	k_2, g/mg min	0.0163	0.0191	0.0152

It can be observed from figure 4 that the Cu(II) ions biosorption on all considered biosorbents is best described by the pseudo-second order kinetics model, and in consequence it can say that the biosorption process is limited by the chemical interactions between Cu(II) ions and functional groups of biosorbents, and these interactions involve two binding sites. On the other hand, comparing the values of the rate constants (Table 2) it can be noted that the Cu(II) ions are easier retained onto lignin, even if the difference between the rate constants calculated for this biosorbent and for the other two, is not significant.

CONCLUSIONS

1. The biosorption potential of some waste biomasses for Cu(II) ions removal from aqueous solution was examined in batch systems as a funtion of initial concentration and contact time.

2. The experimental results were modeled using two isotherm models (Langmuir and Freundlich) and two kinetics models (pseudo-first order and pseudo-second order)

3. The obtained results have indicate that lignin has the higest biosorption potential for Cu(II) ions from aqueous solution, in comparison with marine algae waste and mustard waste.

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REFERENCES

1. **Barakat M.A., 2011-** *New trends in removing heavy metals from industrial wastewater*. Arabian Journal of Chemistry, 4, 361-377.
2. **Bădescu I.S., Negrilă L., Nacu G., Bulgariu L., 2015 -** *Removal of Cu(II) ions from aqueous solution by biosorption on marine algae biomass*. Bulletin of the Polytechnic Institute of Iasi, LXI, 57-66.
3. **Cruz C.C.V., da Costa A.C., Henriques C.A.O., Luna A.S., 2004 -** *Kinetic modeling and equilibrium studies during cadmium biosorption by dead Sargassum sp. biomass*. Bioresource Technology, 91, 249-257.
4. **Demirbas A., 2008 -** *Heavy metal adsorption onto agro-based waste materials: A review*. Journal of Hazardous Materials, 157, 220-229.
5. **Fu F., Wang Q., 2011 -** *Removal of heavy metal ions from wastewaters: A review*. Journal of Environmental Management, 92, 407-418.
6. **Gerente C., Lee V.K.C., Lee P., McKay G., 2007 -** *Application of chitosan for the removal of metals from wastewaters by adsorption - mechanisms and models review*. Critical Reviews in Environmental Science and Technology, 37(1), 41–127.
7. **Gogate P.R., Pandit A.B., 2004 -** *A review of imperative technologies for wastewater treatment II: hybrid methods*. Advanced Environmental Research, 8, 553-597.
8. **Todorciuc T., Bulgariu L., Popa V.I., 2015 -** *Adsorption of Cu(II) from aqueous solution on wheat straw lignin: Equilibrium and kinetic studies*. Cellulose Chemistry and Technology, 49(5-6), 439-447.