OPTIMIZATION OF BIOSORPTION PARAMETERS FOR Cu (II) IONS REMOVAL BY RED AND GREEN MARINE ALGAE BIOMASS

OPTIMIZAREA PARAMETRILOR DE BIOSORBȚIE PENTRU REȚINEREA IONILOR DE Cu(II) PE BIOMASĂ DE ALGE MARINE ROŞII ŞI VERZI

LUCACI Alina-Roxana[1]*, BĂDESCU Iulia Simona[1], BULGARIU Laura[1]
*Corresponding author e-mail: alina-roxana.lucaci@tuiasi.ro

Abstract. *Marine algae are an important biomass resource because of the many properties they have in solving various environmental problems such as the ability to decontaminate wastewater, soil decontamination, soil fertilization, etc. Heavy metal pollution is a problem for the environment. The development of industrial activities has led to increased emissions of heavy metals into the environment, with negative consequences for soils, plants, rivers and waters. Therefore, it is necessary to find appropriate methods that should be environmentally friendly in removing metal ions in a more efficient and inexpensive way. In this paper we optimized the biosorption parameters (pH, initial concentration and contact time) for the retention of Cu (II) ions on algae biomass, using two types of marine algae: a red one Callithamnion corymbosum sp. and a green one - Ulva lactuca sp. from aqueous solution.*
Key words: marine algae biomass, biosorption, Cu (II) ions, experimental parameters

Rezumat. *Algele marine reprezintă o resursă importantă de biomasă datorită numeroaselor proprietăți pe care le au în rezolvarea diferitelor probleme de mediu cum ar fi capacitatea de decontaminare a apelor reziduale, decontaminarea solului, fertilizarea solului etc. Poluarea cu metale grele reprezintă o problemă pentru mediu. Dezvoltarea activităților industriale a condus la creşterea emisiilor de metale grele în mediu, cu consecințe negative asupra solurilor, plantelor, râurilor şi apei. Prin urmare, este necesar să se găsească metode adecvate care ar trebui să fie ecologice în îndepărtarea ionilor metalici într-un mod mai eficient şi mai ieftin. În această lucrare am optimizat parametrii de biosorbție (pH-ul, concentrația inițială şi timpul de contact) pentru reținerea ionilor Cu (II) pe biomasa algelor, folosind două tipuri de alge marine: una roşie- Callithamnion corymbosum sp. şi una verde - Ulva lactuca sp. din soluții apoase.*
Cuvinte cheie: biomasă de alge marine, biosorbție, ioni de Cu(II), parametrii experimentali

INTRODUCTION

Pollution with heavy metals is a problem of great environmental importance. Due to the toxicity, persistence and tendency of accumulation, large

[1] "Gheorghe Asachi" Technical University of Iaşi, Romania

concentrations of heavy metals are found in the environment, becoming an important factor in the degradation of ecosystem quality (Hackbarth *et al.,* 2015). The main source of environmental pollution with heavy metal ions is industrial activity. The development of industrial activities has led to increased emissions of heavy metals into the environment, with negative consequences for soils, plants, rivers and underground waters (Volesky, 2001; Chen, 2004; Aji *et al.*, 2012). Copper and its compounds find a wide range of uses: in sheet metal manufacturing, as catalysts, dyes are used in the paint industry for radiators in electrotechnics and insecticides (Domnez and Aksu, 1999). Therefore, it is necessary to find appropriate methods that should be environmentally friendly and should eliminate heavy metal ions in a more efficient and cheaper way (Oliveira *et al.*, 2013). In recent years, studies of biosorption of metal ions on biological materials have increased significantly (Wang and Chen, 2009). The current trend of specialized research is to find new ecological alternatives and cheap materials for the retention of heavy metal ions through biosorption (Kratochvil and Volesky, 1998).

Marine algae are an abundant and diverse ecosystem. This biomass resource represent a great interest for environmental engineering due to its many properties in solving various environmental problems such as decontaminate wastewater, soil decontamination, soil fertilization (Vilar *et al.*, 2008; Wang and Chen, 2009). Under these conditions, the use of marine algae biomass as biosorbents for the removal of heavy metal ions from aqueous media is in agreement with the actual trends in this filed. It is well known that biosorption of a certain metal ions on certain biosorbent (marine algae biomass, in this case) occurs with maximum efficiency only well-established experimental conditions. Therefore, the find of these experimental conditions, which will ensure the maximum retention efficiency of the biosorption process represent the staring point in such studies. The objective of this study was to find optimal values of the most important biosorption parameters (pH, initial concentration and contact time) for the retention of Cu (II) ions on algal biomass using two types of seaweed: red one - *Callithamnion corymbosum sp.* and a green one - *Ulva lactuca* sp. from aqueous solutions.

MATERIAL AND METHOD

Preparation of biomass

For this study I used seaweed, red *Callithamnion corymbosum sp*. and green algae, *Ulva lactuca sp.* The algae were collected from the Black Sea in 2016. Preparation of the biomass consisted in: washing, drying and grinding into particles with grain-size of 1.0 – 1.5 mm.

Biosorption experiments

To determine the optimal pH, 0.05 g of algae biomass were mixed with 25 ml of Cu (II) solution (25.4 mg/L) with different pH (2.0 – 6.2). After 24 hours, the samples were filtered. To determine the influence of the sorbent dose, different amounts of algae biomass (0.05 - 0.5g) were mixed with 25 ml of Cu (II) solution (25.4 mg/L), and the samples were also filtered after 24 hours. The influence of the initial concentration

was examined in the Cu (II) concentration range of 12 – 178 mg/L, using 0.05 g algae biosorbent for each sample. After 24 hours, the samples were filtered. The influence of contact time was analyzed by adding 25 mL of Cu (II) solution (25.4 mg/L) to 0.05 g algae biomass. The phase's separation was done at certain time intervals, between 5 and 240 min.

Evaluation of biosorption performances

Concentration of Cu (II) ions from aqueous solution was determined spectrophotometrically (with rubeanic acid, 390 nm, 1 cm glass cells, VIS Spectrophotometer YA1407020), using a prepared calibration curve.

The biosorptive performances of algae biomass for Cu (II) ions was evaluated using biosorption capacity (q, mg/g) and removal percent (R, %) calculated from experimental results, according to 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_o, c are initial an equilibrium concentration of Cu(II) in the solution (mg/L), V is volume of solution (L), and m is the mass of algae (g).

RESULTS AND DISCUSSIONS

The pH value for which the sorption process proceeds with maximum efficiency was considered the optimal pH value for retention of metal ions studied on algae biomass. As can be seen from (fig. 1), the amount of metal ions retained on algae biomass (q, mg/g) increases as the initial pH of the aqueous solution increases. In the case of *Ulva lactuca sp.*, the optimum pH is 5.0, where Cu(II) ions are retained approximately 95%, while for *Callithamnion corymbosum sp*., the optimal pH is 4.4, and the removal percent obtained is not greater than 79%.

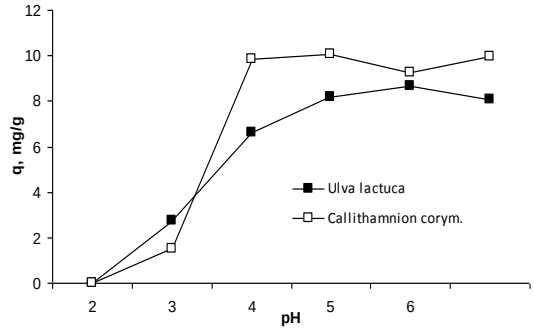

Fig. 1 Influence of initial solution pH

The optimum quantity of biosorbent (fig. 2) was determined on the basis of the values of the quantitative parameters of the biosorption process, being considered the value for which the Cu (II) removal efficiency is maximum.

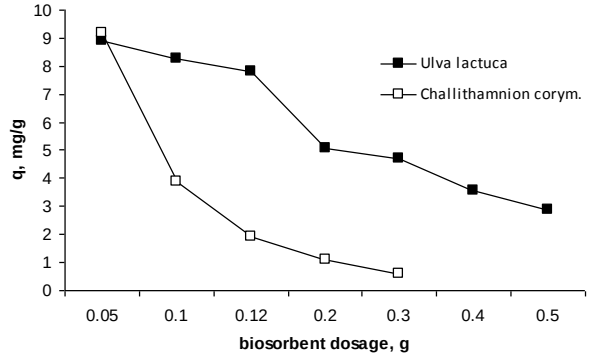

Fig. 2 Influence of biosorbent dosage

Such variation is determined by the increase in the number of active sites (superficial functional groups) with the increase of the quantity of algae biomass used as biosorbent (Ucun et al., 2003). Based on obtained experimental results (fig. 2), the optimal dose of biosorbent was considered 0.05 g for both types of algae biomass.

The increase in the initial concentration of Cu (II) ions over studied concentration range causes an increase of the biosorption capacity (q, mg/g) from 5.19 to 52.26 mg/g for red algae and 3.10 to 57.03 mg/g for green algae (fig. 3).

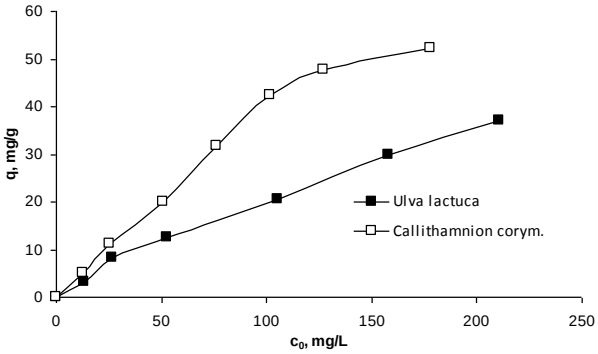

Fig. 3 Influence of the initial concentration

These values correspond to a decrease in the removal percent from 82% to 62% for red algae and 99% to 59% for green algae. Therefore, it can be said that *Ulva lactuca sp*. (green algae biomass) is much more effective in the retention of Cu (II) ions compared to *Callithamnion corymbosum sp.* (red algae biomass).

The influence of contact time has shown that with increasing contact time (Fig. 4), the amount of metal ions retained on the sorbent mass unit increases. The biosorption process is rapid in the initial stage when in the first 5 min the Cu(II) removal percent are higher than 53 % in case of *Ulva lactuca sp*. biomass and 65 % in case of *Callithamnion corymbosum sp.* biomass, respectively. After this initial step, the rate of the biosorption process becomes much slower near the equilibrium, which is obtained after 60 min in the case of *Ulva lactuca sp.* biomass and after 30 min in case of *Callithamnion corymbosum sp.* biomass, respectively.

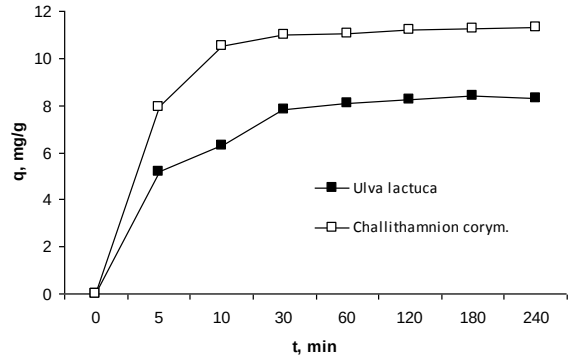

Fig. 4 Influence of contact time

According to these results, *Callithamnion corymbosum sp.* biomass is much more effective in the removal of Cu(II) ions by biosorption, because required a lower minimum contact time (30 min), compared with 60 min in case of *Ulva lactuca sp.* biomass.

In table 1 are summarized the optimal values of the biosorption parameters for the Cu (II) ions removal from aqueous media using *Ulva lactuca sp*. and *Callithamnion corymbosum sp*. algae biomass.

Table 1

Optimal values of biosorption parameters for Cu (II) ions removal on considered algae biomass

Parameters	Ulva lactuca sp.	Callithamnion corymbosum sp.
Initial pH	5.0	4.4
Biosorbent dosage	0.05	0.05
Initial concentration, mg/L	13.18 – 210.93	12.71 – 177.89
Minimum contact time, min	60	30

CONCLUSIONS

Removal of metal ions from wastewater by low-cost biosorption is an effective method that can be successfully applied for wastewater treatment due to the advantages it has. Algae biomass fulfils all the necessary conditions. According to experimental results, the *Ulva lactuca sp*. biomass is much more effective in removal of Cu (II) ions from aqueous solutions compared to *Callithamnion corymbosum sp.* biomass.

Acknowledgments: *This paper was elaborated with the support of grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-III-P4-ID-PCE-2016-0500.*

REFERENCES

1. **Aji B. A., Yavuz Y., Koparal A.S., 2012** - *Electrocoagulation of heavy metals containing model wastewater using monopolar ion electronedes.* Separation and Purification Technology. 86, p. 248-254.
2. **Chen G., 2004** -*Electrochemical technologies in wastewater treatment*. Separation and Purification Technology. 38, p. 11-41.
3. **Donmez G., Aksu Z., 1999** -*The effect of copper (II) ions on the growth an bioaccumulation properties of some yeast*. Process Biochemistry. 35, p.135-142.
4. **Hackbarth F.V., Francielle G., de Sousa A.A., Santos J.C., Boaventura R.A.R., Villar V.J.P., Guelli U. de Sousa S.M.A., 2015** - *Ion exchange prediction model for multi-metal system obtained from single-metal systems using the macroalga Pelvetia canaliculata (Phaeophyceae) as a natural cation exchanger*. Chemical Engineering Journal 260, p. 694-705.
5. **Kratochvil D, Volesky B., 1998** - *Advances in the biosorption of heavy metals*. Trends Biotechnology 16, p. 291–300
6. **Oliveira R. C., HammerP., Guidal E., Taulemesse J.-M., Garcia O. Jr., 2014** - *Characterization of metal-biomass interaction in the lanthanum (III) biosorption on Sargassum sp. Usig SEM/EDX. FTIR, and XPS: preliminary studies*. Chemical Engineering J. 239, p. 381-391.
7. **Ucun H., Bayhan Y.K., Kaya Y., Cakici A., Algur O.F.,2003** -*Biosorption of lead (II) from aqueous solution by cone biomass of Pinus sylvestris*. Desalination, 154(3), p. 233-238.
8. **Vilar V.J.P., Botelho C.M.S., Boaventura R.A.R, 2008** - *Effect of Cu(II), Cd(II) and Zn(II) on Pb(II) biosorption by algae Gelidium-derived materials*. Journal of Hazardous Materials 152, p. 711-720.
9. **Volesky B., 2015** - *Detoxification of metal-bearing effluents biosorption for the next century*, Hydrometallurgy 59, p. 203-216.
10. **Wang J.L., Chen C., 2009** – *Biosorbents for heavy metals removal and their future*. Biotechnology. Advanced. 27, p. 195-226.