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VALORIZATION OF RESIDUAL BIOMASS AS BIOSORBENT: STUDY OF BIOSORPTION BRILLIANT RED DYE FROM AQUEOS MEDIA

BY

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Abstract. A direction for the use of immobilized biomass is to obtain biosorbents to be utilized inbiosorption process of chemical pollutants applied as specific step in the treatment of industrial wastewater. The non-living *Bacillus sp.* and *Aspergillus sp.* biomass immobilized in alginate has been studied for use as a biosorbent to remove Brilliant Red HE-3B organic dye from aqueous medium. Batch experimental studies were focused on determining the influence of certain physical-chemical operating parameters of the biosorption process of the dye, such as: temperature, pH, biosorbent dose, phase contact time, chemical compound concentrations, and dose of biomass.

Keywords: biosorbent; biosorption; organic chemical pollutants; immobilization; residual biomass.

1. Introduction

The textile industry uses large amounts of industrial water and a large variety of synthetic dyes released into the environment (even in small quantities) can be extremely toxic in the aquatic ecosystem. Many methods have

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been used to retain dyestuffs before final effluent reuse or discharge into surface water or another aquatic receptor. These are more or less expensive methods, with varying degrees of efficiency, with different cost / effectiveness ratios (Zaharia and Șuteu, 2012).

Adsorption is a method at which theory and practice return frequently when it comes to retaining dyes. This method is cheap and requires relatively simple installation with an affordable price. It also allows the use of a wide variety of adsorptive materials that ultimately ensure the desired purpose: effluent discoloration and removal of undesirable chemical compounds. Adsorbents can be produced by chemical synthesis, or they can be industrial or agricultural by-products or natural products (Zaharia and Șuteu, 2012). These can be applied in their native state or by carrying out chemical functionalizations on them to improve a number of properties, such as: mechanical strength, form of use, chemical compound retention capacity.

Lately, attention was focused onto the use of bioresources, as by-products from fermentative processes, for developing a new generation of adsorbent materials, that are useful in retaining chemical species (pollutants) with various molecular masses (metal ions, dyes, drugs) (Grassi *et al*., 2019; Souza *et al*., 2018; Argun *et al*., 2017; Camargo *et al*., 2017; Șuteu *et al*., 2012; Gavrilescu, 2010). Bacteria and fungi are used in the biosynthesis industry to produce various metabolites, and also thousands of tons of residual biomass are produced each year (Șuteu *et al*., 2012; Șuteu *et al*., 2013). This non-living biomass could be transformed as eco-friendly biosorbent, since its use provides an alternative and relatively inexpensive method for wastewater treatment. The biomass can be immobilized in sodium alginate in order to obtain granules with the desired diameter particles and an improved mechanical resistance.

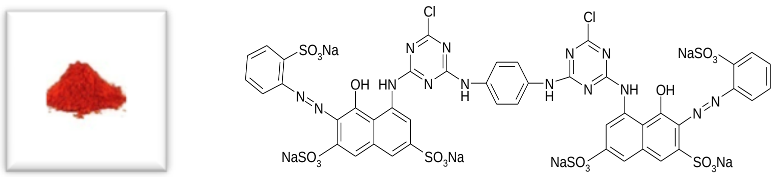
Immobilized biomass will be used for the biosorption of chemical pollutants such as dyes and pharmaceutical waste from aqueous solution for industrial waste water treatment (Argun *et al*., 2017; Bilal *et al*., 2018; Chajnacka, 2010; Saraf and Vaidya, 2015).

In this paper, will be achieved the comparative study about biosorption of Brilliant Red HE-3B dye onto biomass based on *Bacillus sp.* bacteria and *Aspergillus sp*. fungi immobilized in alginate in the form of granules of different sizes. One other purpose was to identify the main parameters that influence the biosorption in order to obtain the optimum biosorption efficiency and a high rate of dyes removal from aqueous media or final effluent discoloration.

2. Experimental Methodology

Materials

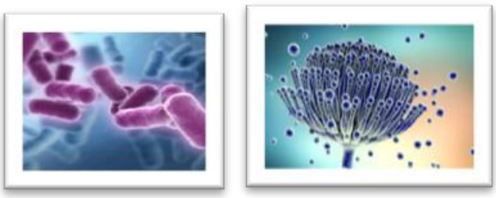
Dyes: Colorant Brilliant Red HE-3B is used in order to study the biosorption in aqueous media as reference model dye (Fig. 1).



a *b*

Fig. 1 − Chemical structure.

Biomass: Non-living *Bacillus sp.* and *Aspergillus sp.* Biomass are illustrated in Fig. 2*a*-*b*.



a *b*

Fig. 2 − (*a*) *Bacillus sp*. Biomass; (*b*) *Aspergillus sp*. biomass.

The respective biomass was immobilized in sodium alginate following a methodology previously described.

The influence of all operating parameters (Fig. 3) will be studied in batch experiments in order to establish the favorable values for this adsorptive process onto immobilized non-living biomass.

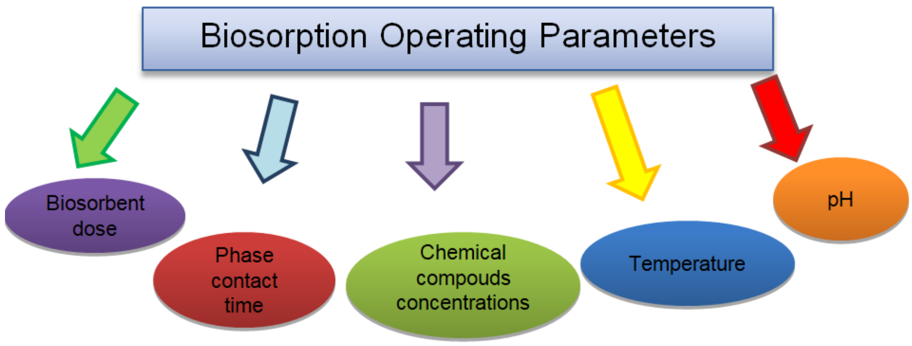


Fig. 3 − Biosorption operating parameters.

Biosorption methodology

The biosorption experiments were performed through a simple batch technique, which consists in contacting different amounts of biosorbent (granules) with dye solutions of different concentrations for a certain contact time (Fig. 4). It has been analysed the influence of physical-chemical operating parameters on the retention of Brilliant Red colorant onto immobilized biomass: pH solution, amount of biosorbent, initial concentration of colorant, chemical compound (dye) concentration, phase contact time, temperature and granules dimensions.

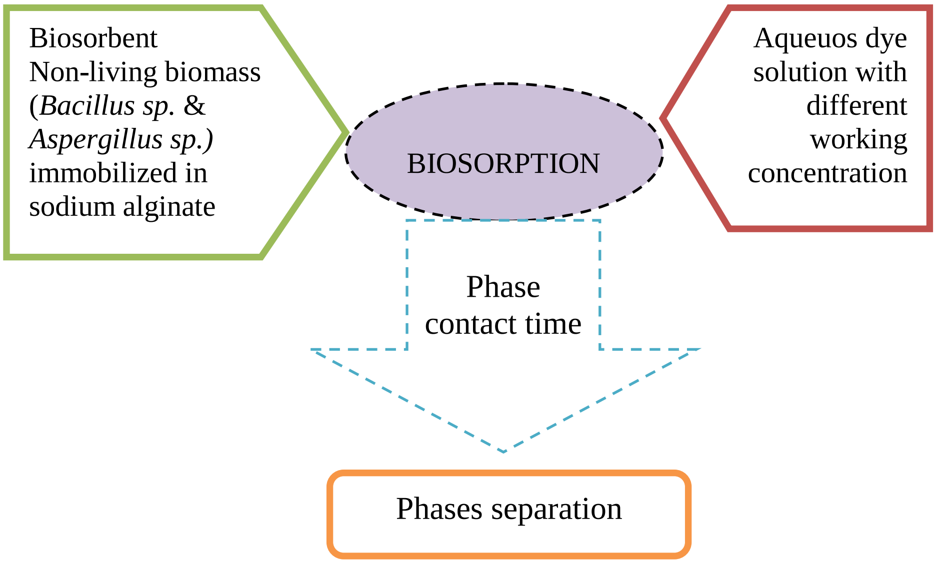


Fig. 4 − Biosorption schematic methodology.

The biosorption efficiency of the non-living biomass immobilized in alginate granules was evaluated by the biosorption capacity (amount of dye adsorbent per 1 gram of biosorbent), [mg/g] (Eq. (1)):

$$q = \frac{C_0 - C}{G} \cdot V \quad [\mathrm{mg \cdot g^{-1}}] \tag{1}$$

and by dye removal, R, [%] (Eq. (2)):

$$R = \frac{C_0 - C}{C_0} \cdot 100 \quad [\%] \tag{2}$$

where: C_0 and C are dye concentration, initial and at equilibrium, [mg/L]; G is the amount of the biosorbent, [g]; V is the volume of the dye solution, [L].

The equilibrium concentration was determined spectrophotometrically by using the UV-VIS digital spectrophotometer, S 104D/WPA model, based on calibration curve method in the field of Lambert Beer Law.

3. Results and Discussions

3.1. Biosorbent Based on *Aspergillus sp.* - Effect of Main Biosorption Operating Parameters

The pH of ***dye solution*** is an important operating parameter of the biosorption process, because his value generates both the biosorbent surface morphology thought availability of the characteristic functional groups into a particular ionic form, and also the ionic form of the species to be retained.

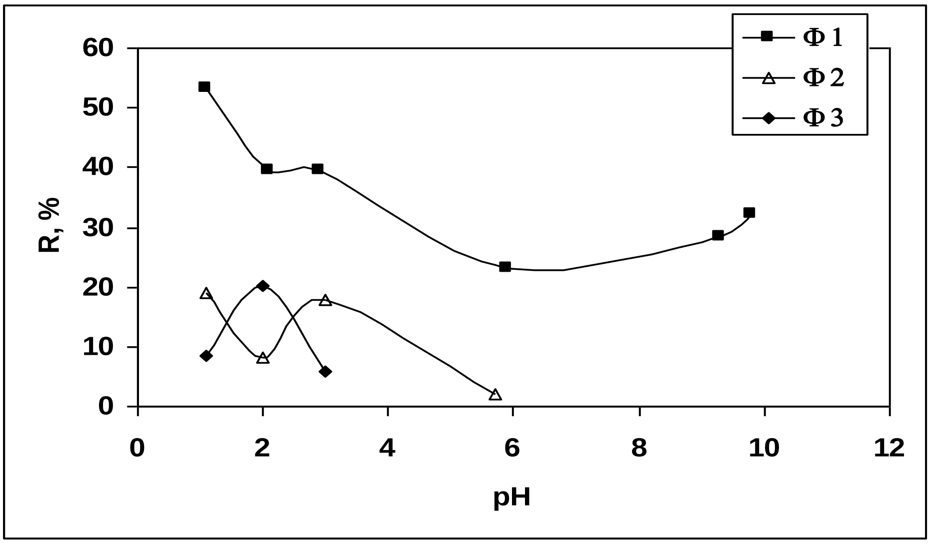
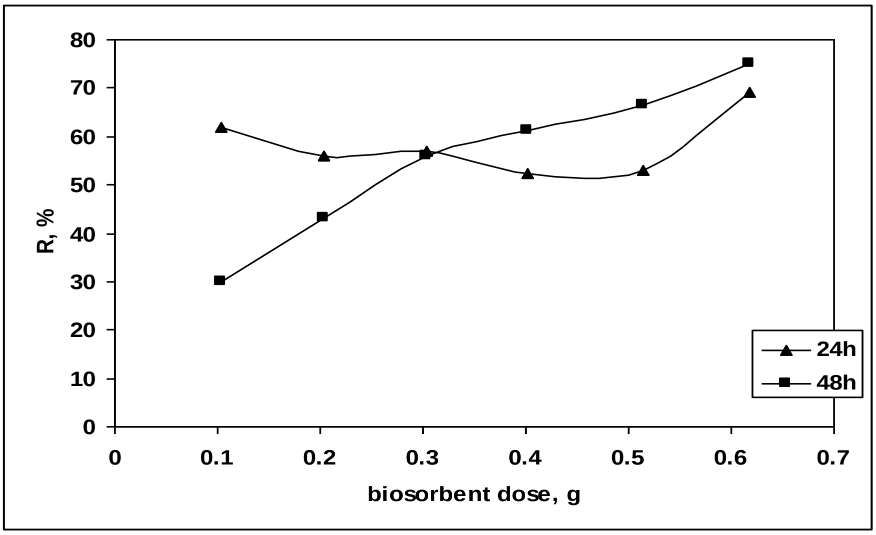


Fig. 5 − Effect of pH and size of granules onto the dye retaining by biosorption onto immobilized Aspergillus *sp.*- based biomass: C_0=54.4 mg/L; $m_{biosorbent}$= 0.2 g; ϕ=1; 2 ; 3 mm; T=18ºC.

It is observed from Fig. 5 that biosorbent granules with diameter ϕ=2 mm and ϕ=3 mm does not confer an uniform behavior because the distribution of biomass is not uniform. Even under these conditions, the dye removal is higher in acid media. The study will continue further with biosorbent granules with ϕ=1 mm.

In the case of fungi, because they are multicellular organisms, there are cell associasions that have prevented obtaining perfectly homogeneous granules. Thus, the biosorbent granules obtained are showed different areas, where the biomass concentration was very high and areas where biomass was not immobilized. This phenomenon was noticed especially in the larger granule diameter and made improper the study in these conditions. Figs. 6-11 summarize the influence of some physical operating parameters, acting individually or in combination of two on biosorption of Brilliant Red HE-3B dye from aqueous media.



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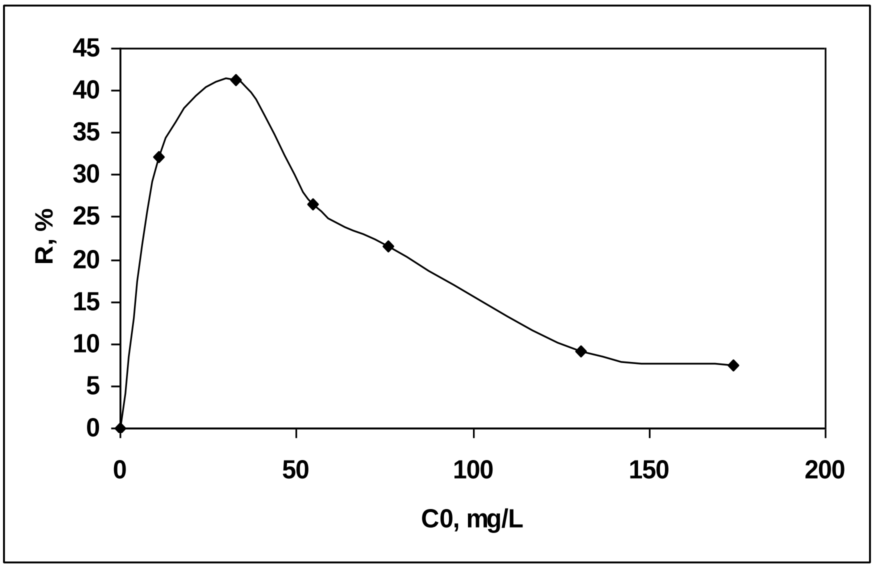


b

Fig. 6 − Effect of biosorbent dose and time *vs.* effect of initial concentration biosorbent (*Aspergillus sp.*), *a*) Effect of biosorbent dose and time, C_0=54.4 mg/L; pH=1; Φ=1 mm; T=18°C;
b) Effect of initial dye concentration, $m_{biosorbent}$=0.1 g; pH=1; Φ=1 mm; T=18°C.

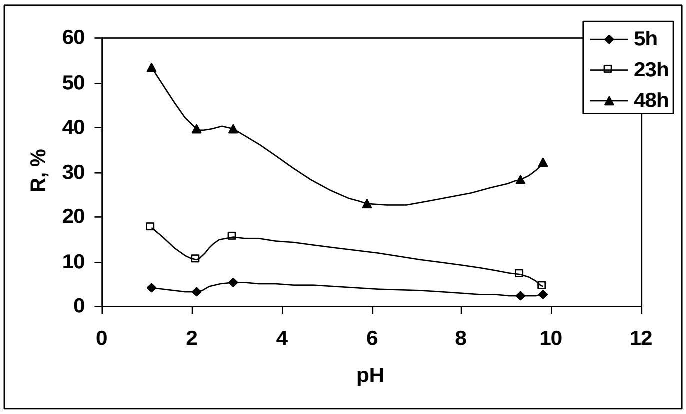


Fig. 7 − Effect of pH solution and phase contact time onto dye removal by immobilized *Aspergillus sp.* - based biomass: C_0=54.4 mg/L; $m_{biosorbent}$=0.2 g; Φ=1 mm; T=18ºC.

The dyeremoval R, [%] increases with contact time increasing, offering better performance in acid medium. However, it was not possible to operate for a long time biosorption because the biosorbent distortion process occurs.

3.2. Biosorbent Based on *Bacillus sp.* - Effect of Main Biosorption Operating Parameters

The dye solution pH is a critical operating parameter because, depending on its value, changes occur in the surface of the biosorbent, but also in the structure of the functional groups of the dye. Its ultimate influence is reduced to a more efficient or less effective biosorption process.

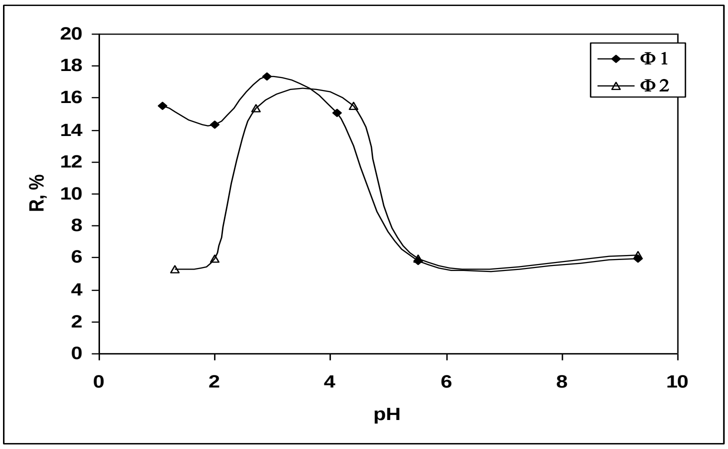
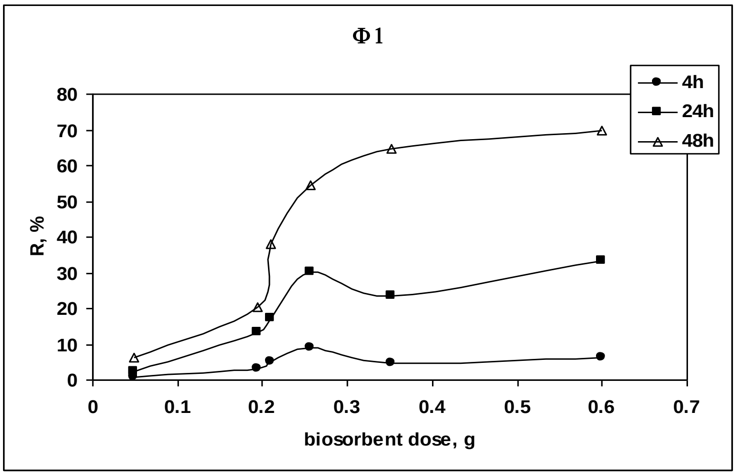


Fig. 8 − Effect of pH solution and the size of biosorbent granules onto dye biosorption onto immobilized *Bacillus sp.* - based biomass: C_0=54.4 mg/L; $m_{biosorbent}$=0.2 g; Φ_1=0.5 mm; Φ_2=1.5 mm; T=18ºC.

The pH rangeused for testingis 1-9.5 because at pH>10-11 are greatly affected the cromophore groups of the dye.



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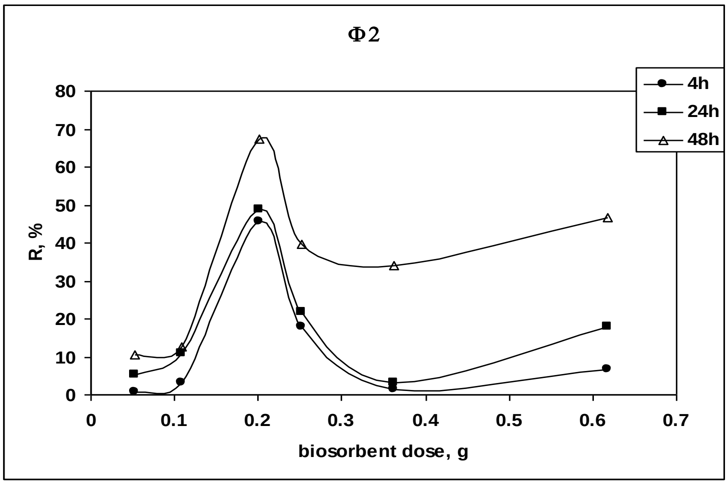
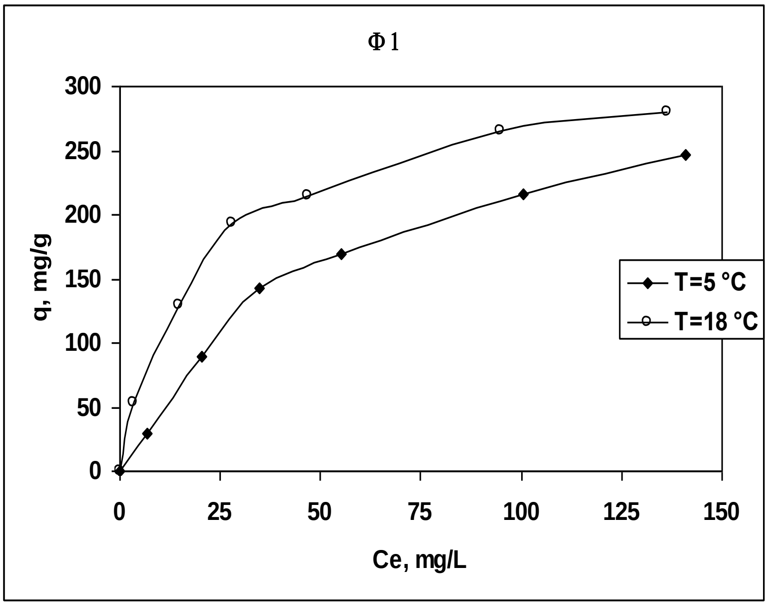


b

Fig. 9 − Effect of pH dye solution, biosorbent dose and phase contact time onto dye biosorption by immobilized *Bacillus sp.* - based biomass: *a*) Φ_1=0.5 mm; C_0=54.4 mg/L; pH=3; T=18ºC; *b*) Φ2=1.5 mm; C_0=54.4 mg/L; pH=1; T=18ºC.

Whatever of the size of the biosorbent granules, it is noted that optimal retention was achieved in acid media. Also, smaller granules have a more efficient behavior due to proving a larger surface for contact between the biosorbent and the dye in the solution. However the contact time, the system's behavior is maintained. The amount of biosorbent of 0.25 g ensures higher dye removal R, [%] in 4-24h.



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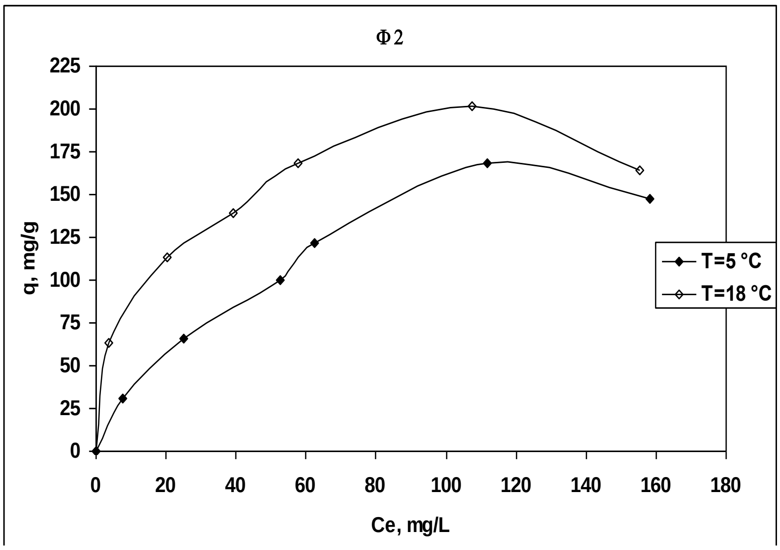
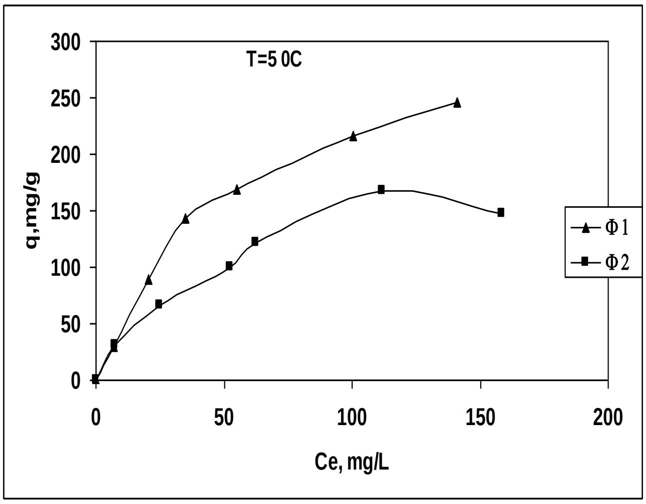


b

Fig. 10 – Effect of temperature and initial dye concentration onto dye removal by immobilized *Bacillus sp.* - based biomass: *a*) Φ_1=0.5 mm; C_0=54.4 mg/L; pH=3; t=24 h; $m_{biosorbent}$=0.25 g; *b*) Φ_2=1.5 mm; C_0=54.4 mg/L; pH=3; t=24 h; $m_{biosorbent}$=0.25 g.

The biosorption process is positively influenced by the highest temperature at which it occurs, suggesting the possibility of an endothermic system (Fig. 11).



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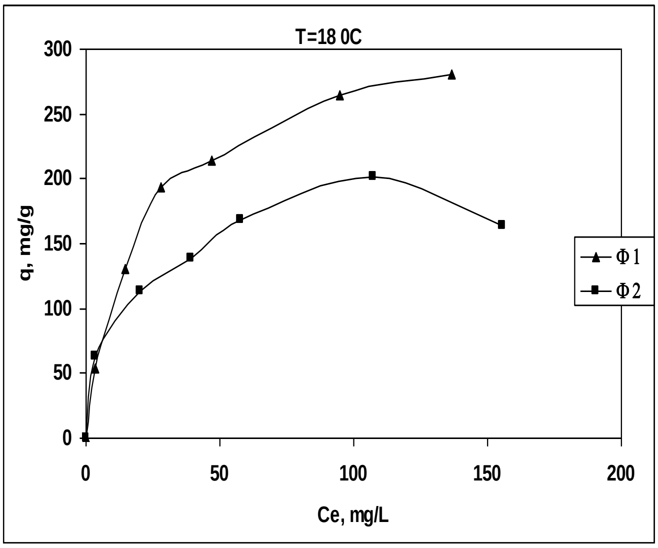

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Fig. 11 − Effect of biosorbent particle size and temperature of process onto dye removal by immobilized *Bacillus sp.* - based biosorbent: C_0=54.4 mg/L; pH=3; $m_{biosorbent}$=0.25 g; Φ_1=0.5 mm; Φ_2=1.5 mm; *a*) T_1=5ºC; *b*) T_2=18ºC.

It can be noticed that biosorbent granules with a smaller dimension Φ_1=0.5 mm, allow obtaining a higher absorption capacity compared to those with Φ_2=1.5 mm. The explanation is given by the mode of distribution of dry mater (biomass) which leads to providing a contact surface (biosorbent-dyes solution) that allows an optimal biosorption.

4. Conclusions

Alginate immobilization of biomass granules leads to preparation of an efficient biosorbent for dye removal from different wastewaters and effluent discoloration.

Smaller biomass granules have a more efficient behavior due to proving a larger surface for contact between the biosorbent and the dye in the solution.

The dye removal R, [%] increases with contact time, keeping better performance in acid medium at T=18ºC and with the amount of biosorbent m= 0.25g.

Regardless the contact time, the system's behavior is maintained. The amount of biosorbent (*i.e*. 0.25g) ensures higher dye removal R, [%] in 4-24 h.

Further studies will be continued with the biomass of Bacillus sp., respectively the study of sorption equilibrium, kinetics and thermodynamics of the process of retaining the Brilliant Red dye in a static or dynamic system.

REFERENCES

Argun Y.A., Karacali A., Calisir U., Kilinc N., Irak H., *Biosorption Method and Biosorbents for Dye Removal from Industrial Wastewater: A Review,* Int. J. Adv. Res. **5**, *8*, 707-714 (2017).

Bilal M., Rasheed T., Sosa-Hernandez J.E., Raza A., Nabeel F., Igbal H.M.N., *Biosorption: An Interplay between Marine Algae and Potentially Toxic Elements – A Review*, Mar. Drugs, **16**, *2*, doi: 10.3390/mad16020065 (2018).

Camargo de Castro K.C., Cossolin A.S., Oliveira dos Reis H.C., Beraldo de Morais E., *Biosorption of Anionic Textile Dyes from Aqueous Solution by Yeast Slurry from Brewery*, Braz. Arch. Biol. Technol., v.**60**: e160411 (2017).

Chajnacka K., *Biosorption and Bioaccumulation – The Prospect for Practical Applications*, Environmental International, **36**, *3*, 299-307 (2010).

Gavrilescu M., *Environmental Biotechnology: Achievements, Opportunities and Chalenges*, Synamic Biochemistry, Process Biotechnology and Molecular Biology, **4**, *1*, 1-36, Global Science Book (2010).

Grassi P., Reis C., Drumm F.C, Georgin J., Tonato D., Escudero L.B., Kuhn R., Jahn S.L., Dotto G.L., *Biosorption of Crystal Violet Dye Using Inactive Biomass of the Fungus Diaporthe Schini*, Water Sci. Technol., **79,** *4*, 709-717 (2019).

Saraf S., Vaidya V.K., *Comparative Study of Biosorption of Textile Dyes Using Fungal Biosorbents*, Int. J. Curr. Microbiol. App. Sci., **2**, 357-365 (2015).

Souza P.S.C., Santos J., Souza A.R., Spessato L., Pezoti O., Alves H.J., Colauto N.B, Almeida V.C., Dragunski D.C., *Biosorption of Reactive Red-120 Dye onto Fungal Biomass of wild Ganoderma Stipitatum*, Desalination and Water Treatment, **102**, 280-288 (2018).

Şuteu D., Zaharia C., Blaga A.C., *Chap. 12*, *The Action of Microorganisms from Organic Pollutants in Water, Air, Soil*, in "Current Topics, Concepts and Research Priorities in Environmental Chemistry", Vol. **II**, Zaharia (Ed.), Edit. Univ. A. I. Cuza, Iași, Romania, 259-274, 2013.

Şuteu D., Zaharia C., Blaga A.C., *Chap. 10, Biosorption – Current Bioprocess for Wastewater Treatment*, in "Current Topics, Concepts and Research Priorities in Environmental Chemistry", Vol. **I**, Zaharia (Ed.), Edit. Univ. A. I. Cuza, Iaşi, Romania, 221-244, 2012.

Zaharia C., Şuteu D., *Chap. 3, Textile Organic Dyes – Characteristics, Polluting Effects, and Separation/Elimination Procedures from Industrial Effluents. A Critical Overview*, in "Organic Pollutants Ten Years after the Stockholm Convention - Environmental and Analytical Update", T. Puzyn, A. Mostrag-Szlichtyng (Eds.), INTECH Publisher, Rijeka, Croatia, 57-86, 2012.

VALORIFICAREA BIOMASEI REZIDUALE CA BIOSORBENT: STUDIUL BIOSORBŢIEI COLORATULUI BRILLIANT RED DIN MEDIU APOS

(Rezumat)

O direcţie pentru utilizarea biomasei imobilizate este obţinerea de biosorbenţi pentru a fi folosiţi într-un proces de biosorbţie a poluanţilor chimici aplicat în epurarea apelor uzate industriale. Biomasa moartă de *Bacillus sp.* şi *Aspergillus sp.* imobilizată în alginat de sodiu a fost studiată în scopul utilizării ca biosorbent pentru îndepărtarea colorantului organic Brilliant Red HE-3B din mediu apos. Studiile experimentale, efectuate în condiţii statice, s-au axat pe stabilirea influenţei anumitor parametri operationali fizico-chimici ai procesului de biosorbţie a colorantului, cum ar fi: temperatura, pH-ul, doza de biosorbent, timpul de contact al fazelor, concentraţiile compuşilor chimici reţinuţi şi doza imobilizată de biomasă.