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Biosorption of reactive dyes from aqueous media using the *Bacillus* sp. residual biomass

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ABSTRACT

The goal of this work is to make use of residual biomass that, although it results in large quantities from biotechnological processes, is not reported to be valorized in dye adsorption processes, except in a few applications. The biosorption potential of *Bacillus* sp. residual biomass in a textile dye removal (i.e. reactive Brilliant Red HE-3B dye) from aqueous media was studied. The waste biomass, resulting from a process of removing fatty acids from wastewater, was immobilized in the sodium alginate and used for biosorption of the dye from aqueous solution using the batch system. Experimental data were analyzed using Freundlich, Langmuir (I and II), and Dubinin–Radushkevich adsorption isotherm models. Equilibrium data were best fitted by Langmuir I isotherm with a biosorption capacity of about 588.235 mg/g at 20°C. Also, the results confirm that the biosorption process is carried out with much better results for the smaller biosorbent granules (Φ1 = 0.5 mm). The obtained results in the batch system revealed that the reactive dye biosorption process using immobilized residual biomass is a physical-chemical process corresponding to good results at room temperature (20°C–25°C). Thus, this residual biomass is a promising adsorptive material for the biosorption of reactive dyes from aqueous media.

Keywords: Aqueous medium; *Bacillus* sp.; Biosorption; Reactive dye removal; Immobilization; Residual biomass

1. Introduction

Biomass includes all forms of plant or animal material, grown on the surface of the earth, air, water and materials produced by biological growth [1–3], representing the biodegradable part of products, waste, and residues from agriculture, including vegetal and animal matters from forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste. Thus, biomass sources are extremely diverse, including forest waste, wood processing waste, plant residues from agriculture, the food and biosynthesis industry, animal residues, and special crops with high growth rates. On both international and European Union policy level, a key aim of clean biomass production management is also the recovery of waste biomass, because it represents a valuable resource of nutrients (Fig. 1) [4–8].

With a very widespread in nature (in soil, water, air, on the surface and inside objects, products of plant and animal organs), microorganisms participate actively in the circuit

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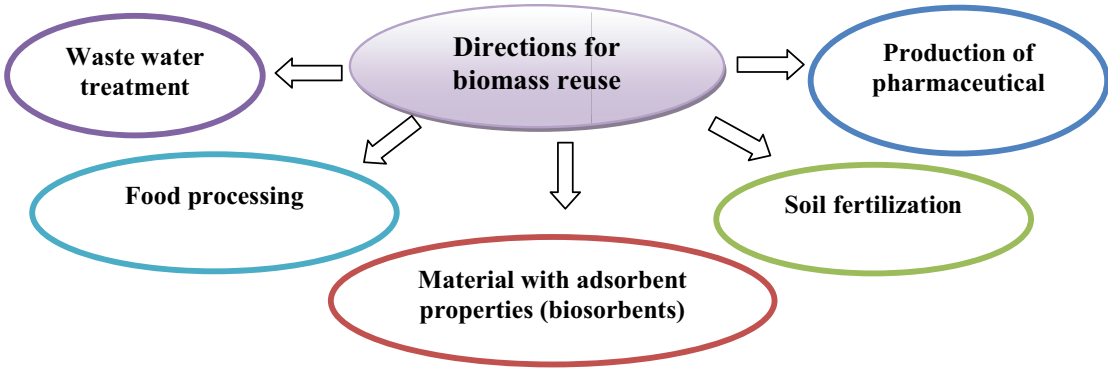

Fig. 1. General directions for waste biomass reuse.

of matter in nature, in the formation and fertilization of the soil, in the processing and conservation of agro products, in the manufacture of the pharmaceuticals and biosynthesis products (organic acids, alcohols, ketones, antibiotics, vaccines, vitamins, enzymatic preparations), wastewater treatment, pollution control, and etc. [9].

Lately, the attention is directed to the residual biomass, described as a by-product from the biosynthesis process (pharmaceutical or food industry), and their use in immobilized form as biosorbent is an efficient way of converting this by-product (in some cases even waste) into a value-added one for the environment. Immobilization on inert support ensures the efficiency and ease of biomass manipulation. The advantages of immobilizing active microorganisms on solid supports are various [9,10]:

- Increased efficiency in relation to cell suspensions;
- Possibility of maintaining an important concentration of active microbial biomass on support;
- Protection of microbial cells from the toxic action of organic compounds that are present in the environment;
- Ease of handling active immobilized biomass, throughout the entire technological process.

The supports used for immobilization can be (i) inorganic (zeolite, diatomite, clay, anthracite, porous glass, activated carbon, etc.) characterized by thermostability and resistance to microbial degradation; (ii) organic (cellulose, wood sawdust, delineated sawdust, etc.). They also include a series of natural and synthetic polymers. Experimentally, several synthetic derivatives (acrylamide, polyurethane, polyvinyl, resins) and natural polymeric derivatives of polysaccharides (alginate, carrageenan, agar, agarose, and chitosan) are used. The most commonly used polymers are the natural ones, such as alginates and carrageenan, but they are less stable in wastewater than synthetic polymers.

The immobilization of biomass on certain types of substrates leads to the obtaining of new materials with adsorbent properties that can be used in biosorption processes applied for the wastewater treatment, water treatment, treatment of polluted soils [1]. These types of biosorbents have a number of advantages over conventional adsorbents, that is, microbial biomass does not generate huge quantities of sludge, it has great genetic diversity, metabolic versatility, and abundance [1,11].

In the biosorption processes applied in wastewater treatment, biosorbents, based on immobilized biomass, have proven efficiency in retaining inorganic species [12–14] and organic species [15–21].

In this context, these types of biosorbents appear as a viable alternative to the remediation of pollution problems caused by industrial dyes, which represent important pollutants of surface waters and other water resources or aqueous environments. Although, these are present in the domestic wastewater in relatively low concentrations, the industrial dyes, coming mainly from the textile or chemical synthesis industry, are included in the category of refractory pollutants due to the effects they produce: decomposition into products with carcinogenic potential, affecting the aquatic life.

For this reason, many methods for their removal have been proposed: adsorption/sorption and biosorption processes, sonolysis, electrocoagulation [22–24], among others. The absorption remains, however, a process very often addressed in solving this problem, due mainly to an attractive relationship between the costs involved and the process efficiency. The development of new types of materials with adsorptive properties comes in support of adsorption application for the removal of dyes from wastewater.

Taking as a starting point in our previous study [25], this paper continues the investigation of a reactive dye biosorption process onto residual biomass immobilized in sodium alginate in order to acquire precious information regarding the equilibrium and thermodynamics of this biosorption process. To achieve this objective, the work reports the experimental results using residual biomass of *Bacillus* sp. immobilized in alginate as a potential biosorbent for the removal of anionic dye Brilliant Red HE-3B from aqueous solutions using the batch system. The experimental data were analyzed using different equilibrium isotherm models in order to estimate the quantitative characteristic parameters, thermal effect, and to assess the mechanism of biosorption.

2. Materials and methods

2.1. Materials

Bacillus sp. are members of the family *Bacillaceae*, a group of gram-positive, rod-shaped, aerobic or facultatively anaerobic, saprophytic, sporulating bacteria commonly isolated

from dust, soil, air, and water. The mixture used in the experiment comprises in equal ratios the following strains: *Bacillus subtilis*, *Bacillus megaterium*, *Bacillus licheniformis*, and *Bacillus amyloliquefaciens*, and it was used for the removal of fats, oils, and grease (solid waste) from wastewater, at 35°C and 150 rpm, in an aerobic system for 96 h. At the end of the process, the biomass was separated by centrifugation (8,000 rpm), dried at 80°C, and immobilized by cell inclusion into sodium alginate. The two solutions used for the immobilization were: 1% concentration sodium alginate (prepared in distilled water at 70°C), and 0.2% calcium chloride (prepared in distilled water at 5°C). The residual biomass concentration was 5%, mixed with the sodium alginate solution and dripped into the calcium chloride solution through two different capillaries, thus obtaining spherical beads with Φ1 = 0.5 mm/Φ2 = 1.5 mm diameter [25].

The Brilliant Red HE-3B (Procion Red HE-3B, C.I. Reactive Red 120) from Bezema – BRed), a bifunctional monochlorotriazine reactive dye (MW = 1463, λ_{max} = 530 nm) with chemical structure, showed in Fig. 2, was selected for this study. Stock solution (with a concentration of 500 mg dye/L) was prepared using the commercial form of the dye (salt of analytical reagent grade) and distilled water; the working solutions were obtained from the stock solution by appropriate dilution with distilled water.

2.2. Batch biosorption equilibrium studies

The biosorption equilibrium studies were performed using 100 mL-Erlenmeyer flasks in which they got in contact amounts of 0.2 g of immobilized biomass (8 g/L) with 25 mL of dye solutions with different initial known dye concentrations (11–176.65 mg/L) and three pH values (adjusted with 1 N HCl solution), at a constant desired temperature (in a thermostatic bath). It was worked at three different temperatures (5°C, 20°C, and 45°C) with a contact time of phases about 24 h. After reaching the equilibrium times, the dye content in the supernatant was determined spectrophotometrically using a JK-VS-721N VIS Spectrophotometer at maximum dye wavelength of 530 nm.

The biosorption capacity of the biomass was estimated using the amount of adsorbed dye (q, mg of dye/g of biomass) calculated as follows:

$$q = \frac{C_0 - C}{G} \cdot V \tag{1}$$

where C_0 and C are the initial and the equilibrium (residual) concentration of dye in solution (mg/L), G is the amount of biomass (g) and V is the volume of solution (L).

The equilibrium data were analyzed using three of the most known sorption equilibrium models (Freundlich, Langmuir, and Dubinin–Radushkevich) from scientific literature and presented in Table 1 [26].

2.3. Thermodynamic of biosorption

The characteristic thermodynamic parameters were determined using known equations [27]:

$$\Delta G = -RT \ln K_L \tag{2}$$

$$\ln K_L = -\frac{\Delta H^\circ}{\mathrm{RT}} + \frac{\Delta S^\circ}{R} \tag{3}$$

where ΔG is free energy (kJ/mol), ΔH is enthalpy (kJ/mol) and ΔS is biosorption entropy changes (kJ/mol K), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature of the solution (K) and K_L is the values of Langmuir constant (L/mol).

3. Results and discussion

Previous studies have concluded that the biosorption of Brilliant Red HE-3B dye onto *Bacillus* sp. biomass immobilized in alginate is satisfactory under the following conditions: smaller biomass granules have a more efficient behavior (Φ1 = 0.5 mm), pH = 3, the contact time of 24 h, the temperature of 20°C and the amount of biosorbent, m = 0.2 g [25].

In the present study the description and interpretation of the biosorption equilibrium were approached in order to determine the characteristic quantitative parameters that describe the process and which allow, subsequently, to carry out optimization analysis and thermodynamic calculation, respectively the identification of the dye retention mechanism on immobilized biomass.

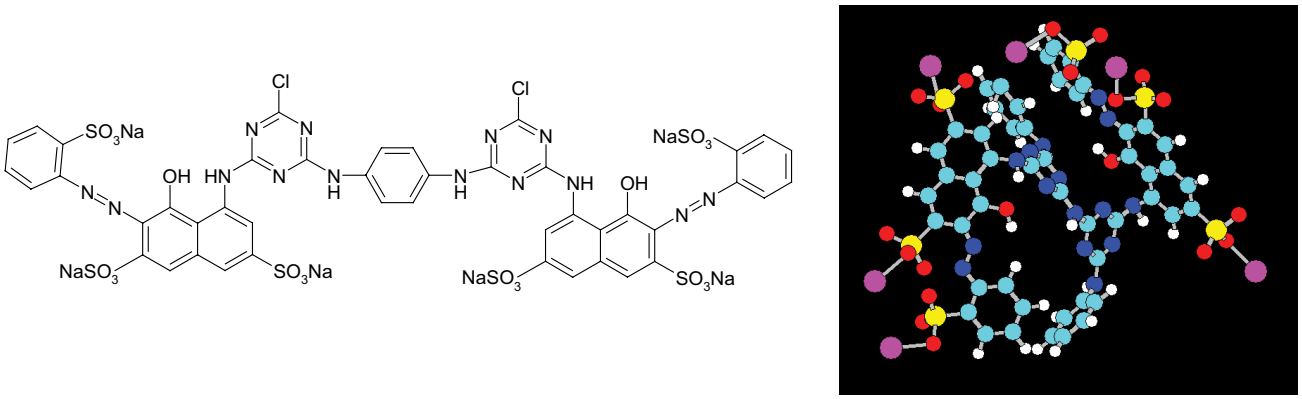

Fig. 2. Reactive dye Brilliant Red HE-3B (C.I. Reactive Red 120).

Table 1
The characteristics of the selected isotherm models

Adsorption isotherm model/assumption	Nonlinear/linear form of the equation	Characteristics
Freundlich: surface heterogeneity and an exponential distribution of active sites of the adsorbent.	$q = K_F \cdot C^{1/n}$ $\log q = \log K_F + \frac{1}{n}\log C$	K_F and $1/n$ – constants associated with the adsorption capacity and intensity (efficiency), respectively; favorable adsorption corresponds to a value of $1 < n < 10$.
Langmuir: maximum adsorption corresponds to a monolayer of solute molecules on the adsorbent surface, containing a finite number of energetically equivalent sites.	$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$ $L1: \frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0} \cdot \frac{1}{C}$ $L2: \frac{C}{q} = \frac{1}{q_0 \cdot K_L} + \frac{C}{q_0}$	q_0 is the maximum amount of adsorbed solute (mg/g) and K_L is the constant related to the binding energy of solute (L/mg).
Dubinin–Radushkevich: nature of the adsorption process could be physical or chemical: $E > 8$ kJ/mol characterizes a physical adsorption mechanism and values between 8 and 16 kJ/mol indicates an ion-exchange mechanism.	$q = q_0 \exp\left(-B \cdot \varepsilon^2\right)$ $\ln q = \ln q_0 - B\,\varepsilon^2$ $\varepsilon = RT \ln\left(1 + \frac{1}{C}\right)$ $E = \frac{1}{\sqrt{2B}}$	q_D is the maximum adsorption capacity (mg/g); B is the activity coefficient related to mean adsorption energy; ε is the Polanyi potential and E is the mean free energy of adsorption (kJ/mol).

The equilibrium isotherm, defined as the amount of sorbate retained by the unit of sorbent (q, mg/g) as a function of the sorbate concentration at equilibrium in the liquid phase (C, mg/L), could be described by a lot of isotherm models, in order to determine the characteristic quantitative parameters and to obtain initial information about the involved mechanism.

The experimental and modeled data with proposed isotherm models (characterized in Table 1) of reactive dye Brilliant Red HE-3B on *Bacillus* sp. biomass immobilized in alginate are presented in Fig. 3.

The characteristics parameters of isotherms related to each sorption model (Freundlich, Langmuir I and II, and Dubinin–Radushkevich), calculated from the intercepts and slopes of the corresponding linear plots (Fig. 4) are presented in Table 2. In order to appreciate which model describes better the biosorption process of reactive dye Brilliant Red HE-3B onto *Bacillus* sp., at this stage, the selection was performed based on the values of the correlation coefficients, R^2.

Analyzing the data summarized in Table 2, the following conclusions can be drawn:

- The values of Freundlich quantitative parameters, K_F and n decrease with increasing of the temperature, showing that the biosorption process is favorable at relatively low temperature;
- The values of the correlation coefficients higher than 0.99 show that the Langmuir model was more suitable to describe the biosorption process. Of the two forms of the Langmuir model, the model I is best suited (achieving a much better correlation degree of data, R^2) than model II.
- The values obtained for the maximum biosorption capacity, from Langmuir I model (q_0, mg/g) confirm that the biosorption is underway with much better results using the smaller size biosorbent granules (Φ1 = 0.5 mm) which ensures better interaction between the dye and biosorbent molecules.
- The values of the biosorption capacity (q_0, mg/g) increases slightly with increasing temperature (despite the alloying of graphical isothermal sleep). This behavior suggests that the temperature does not have a significant influence on the biosorption process, the practical implementation at ambient temperature (20°C–25°C) being preferred. The variant is also ensuring a reduction of the experimentation costs.
- The mean free adsorption energy, E, calculated by Dubinin–Radushkevich equation, was used to estimate the nature of the biosorption process (physical or chemical). The obtained values are around 10 kJ/mol, values characteristic for a physisorption process of the dye on the immobilized biomass.
- Also, the values of the biosorption capacity in the Dubinin–Radushkevich equation, q_0 (represent the total specific meso- and macropore volume of the biosorbent, mg/g), are more than q_0 value resulted using the Langmuir I isotherm model, for all three temperatures. The explanation could be given by considering a porous structure of the biosorbent.

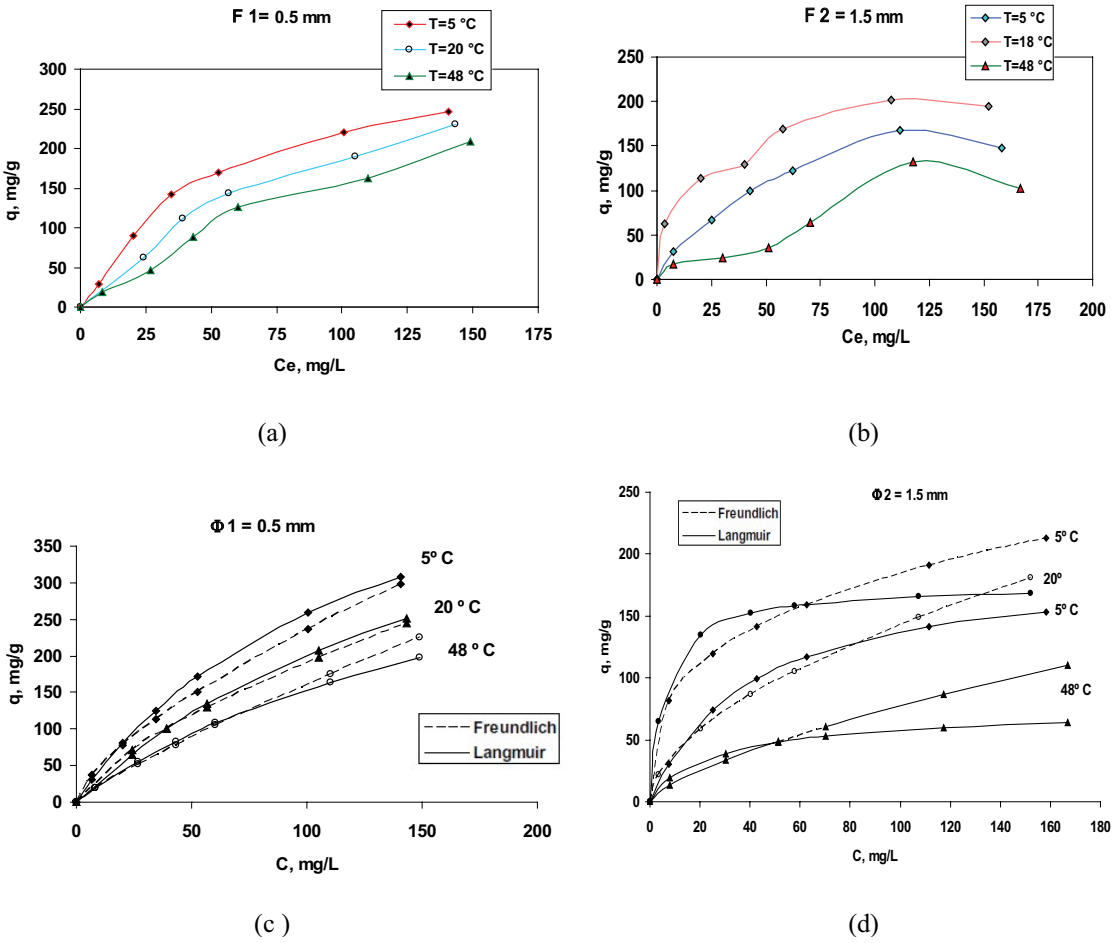

Fig. 3. Biosorption experimental (a and b) and modelled (c and d) isotherms of Brilliant Red HE-3B dye on *Bacillus* sp. residual biomass immobilized in alginate. Conditions: pH = 3; contact time = 24 h; biosorbent concentration = 8 g/L; diameter of granules: Φ1 = 0.5 and Φ2 = 1.5 mm.

The value obtained for the biosorption capacity, according to the Langmuir I model is comparable with other adsorption capacities reported in the literature for different types of biomass in the free or immobilized state on various supports for removal of dyes from aqueous medium (Table 3).

3.3. Thermodynamic parameters

To evaluate the effect of temperature on the Brilliant Red HE-3B dye biosorption onto *Bacillus* sp. immobilized in the sodium alginate and to establish the nature of the biosorption process (that could be physical or chemical but without a clear demarcation), thermodynamic parameters were determined (Table 4) from the values of Langmuir constant, K_L (L/mol), and the Eqs. (2) and (3) [32,33].

Analyzing the data from Table 4, some conclusions can be highlighted:

- The negative values of Gibbs free energy, $\Delta G°$, indicate that the anionic dye biosorption on studied immobilized residual biomass is spontaneous. According to the information in the literature ($\Delta G°$ between –20 and 0 kJ/mol indicates a physical mechanism of adsorption), the values obtained for $\Delta G°$ suggest a physical mechanism for the studied biosorption process, according to the preliminary indications indicated by mean free adsorption energy, E, calculated by Dubinin–Radushkevich equation.
- The negative value of adsorption enthalpy ($\Delta H°$) computed from the slope of linear dependence $\ln K_L$ vs. $1/T$ underlines the exothermic nature of dye biosorption. The value obtained for $\Delta H°$ is insufficient for chemical adsorption (which should be in the order of –40 to –800 kJ/mol [32]). Information in this field specifies that both the physical and chemical forces can be involved in the biosorption process on a solid surface, but the energy requirement is different (thus, for physical forces as van der Waals: 4–10 kJ/mol, hydrophobic bond: 5 kJ/mol, coordination bond: 40 kJ/mol, dipole bond forces: 2–29 kJ/mol and for chemical forces the energy need would be >60 kJ/mol [33]). Thus, the value obtained for the biosorption of Brilliant Red HE-3B dye on residual *Bacillus* sp. immobilized in alginate biosorbent suggests, in agreement with adsorption energy at low coverage deduced from Dubinin–Radushkevich equation, that the process is more physical than chemical.

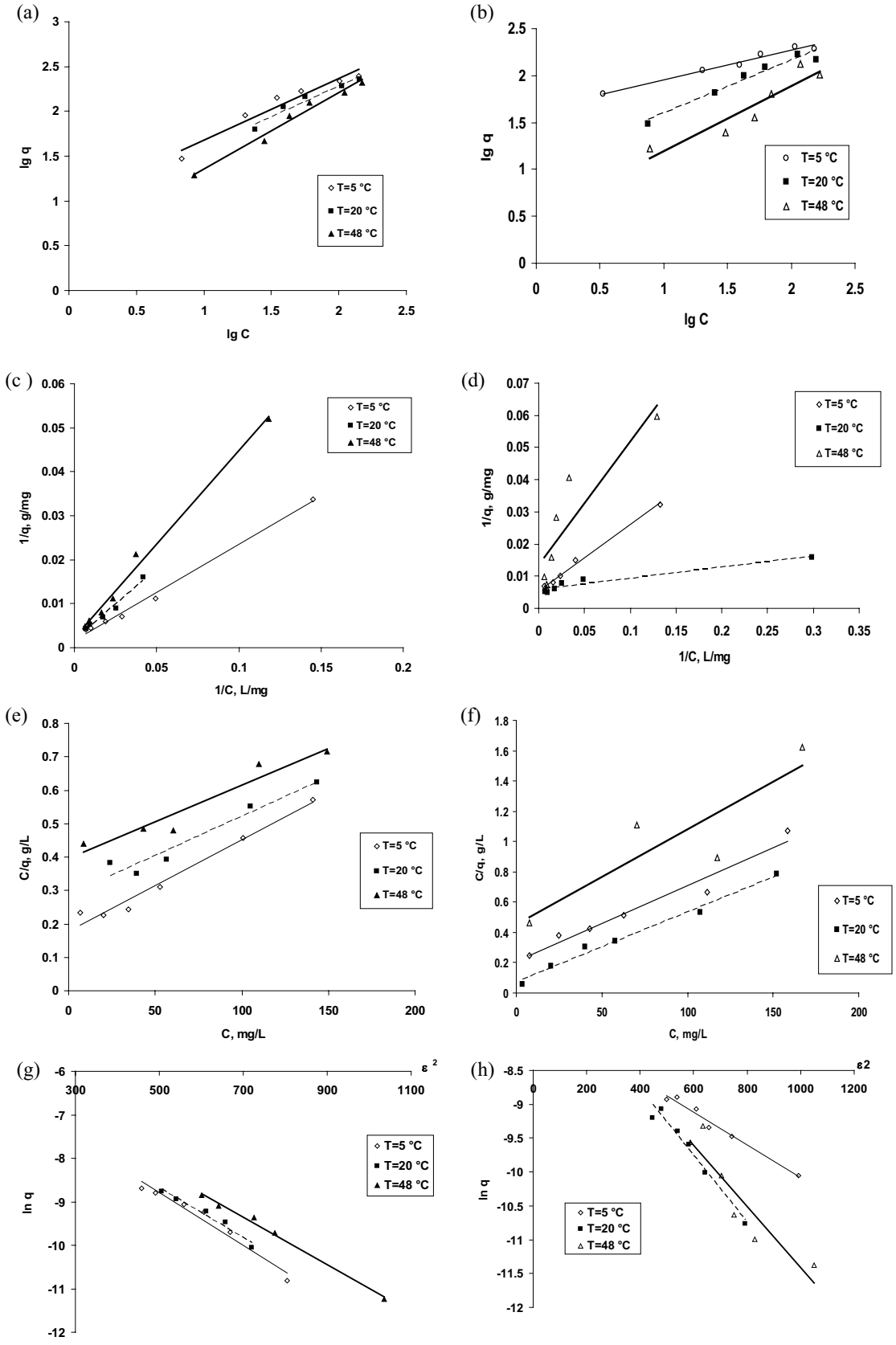

Fig. 4. The linearized form of Freundlich (a and b), Langmuir I (c and d), Langmuir II (e and f) and Dubinin–Radushkevich (g and h) plots for the anionic dye Brilliant Red HE-3B biosorption on *Bacillus* sp. residual biomass immobilized in alginate. Conditions: pH = 3; contact time = 24 h; biosorbent dose = 8 g/L; diameter of granules: Φ1 = 0.5 mm (a, c, e, g) and Φ2 = 1.5 mm (b, d, f, h) at three temperatures: 5°C, 20°C, and 48°C.

Table 2
Characteristic quantitative parameters for the biosorption of anionic dye Brilliant Red HE-3B onto *Bacillus* sp. immobilized in alginate

Isotherm	Φ1 = 0.5 mm			Φ2 = 1.5 mm		
	278 K	293 K	321 K	278 K	293 K	321 K
Freundlich						
K_F ((mg/g) (L/mg)$^{1/n}$)	9.7701	8.1520	3.1920	43.4610	10.9496	3.2140
n	1.448	1.4594	1.1755	3.1840	1.7915	1.4480
R^2	0.9429	0.9543	0.9793	0.9772	0.9531	0.8655
Langmuir I ($1/q = f(1/C)$)						
q_0 (mg/g)	588.2350	588.2350	454.5450	192.3080	175.4380	74.6270
K_L (L/g)	0.007802	0.005211	0.00515	0.02495	0.1633	0.03474
R^2	0.9941	0.9740	0.9967	0.9916	0.9371	0.8028
Langmuir II ($C/q = f(C)$)						
q_0 (mg/g)	370.370	434.783	454.545	200.000	217.391	256.410
K_L (L/g)	0.01515	0.00802	0.00554	0.02382	0.06117	0.00466
R^2	0.9763	0.9393	0.9260	0.9579	0.9863	0.3119
Dubinin–Radushkevich						
q_0 (mg/g)	4,623.0026	4,393.1	5,983.7	691.7	1,617.0	1,466.0
B (mol^2/kJ^2)	0.0061	0.0057	0.0055	0.0024	0.0049	0.0054
E (kJ/mol)	9.053	9.366	9.535	14.434	10.1015	10.541
R^2	0.9615	0.9632	0.9917	0.9786	0.9659	0.8451

Table 3
Some applications of biomass, in the free or immobilized state on various supports, as adsorbents in removal of dyes

Biosorbent	Dye	Biosorption capacity, mg/g	References
Bacillus subtilis	Methylene Blue	169.49 mg/g at 298 K	[27]
Cyanthillium cinereum (L) and *Paspalum maritimum* (PMT)	Methylene Blue	76.335 and 56.1798 mg/g, respectively	[28]
Neurospora sitophila immobilized on the green type biomatrix of *Phragmites australis* spongy	Basic Blue	154.756 mg/g	[29]
Encapsulated iron oxide nanoparticles (NPs) and *Agrobacterium fabrum* strain SLAJ731 in calcium alginate	Methylene Blue	91.1 mg/g	[30]
Lentinus concinnus and *Lentinus concinnus* immobilized in polyvinyl alcohol/polyethylene oxide hydrogels (PVA/PEO)	Reactive Yellow 86	190.2 and 87.6 mg/g, respectively	[31]
Bacillus subtilis sp. immobilized in sodium alginate	Brilliant Red HE-3B	588.235 mg/g	This study

4. Conclusions

The results of this study show that the tested residual biomass of *Bacillus* sp. immobilized in sodium alginate is worthy to be considered as a potential biosorbent for the removal of Brilliant Red HE-3B anionic dye from aqueous solutions at pH 3.

The equilibrium biosorption data, analyzed with Freundlich, Langmuir, and Dubinin–Radushkevich models, are better described by Langmuir I isotherm model, and the obtained biosorption capacity value is 588.235 mg/g at 20°C.

The values of the mean free energy of adsorption (E, kJ/mol) obtained from the Dubinin–Radushkevich model around 9 kJ/mol revealed a physical mechanism for the anionic dye biosorption on immobilized biomass, that was confirmed also, by the values of the thermodynamic parameters (ΔH, kJ/mol).

The values of thermodynamic parameters confirm also the feasibility and the endothermic behavior of the biosorption process.

The results that were obtained in the present paper and the great advantages of the immobilized residual biomass (easily to handling and the possibility to reuse the residual biomass) suggests that the biosorption studies can be extended by using this type of biosorbent to persistent organic micropollutants (micro-POPs), such as drug residues with a molecular weight up to 400–500 g/mol or heavy metal ions present in various aqueous environments.

Table 4
Thermodynamic parameters of the adsorption of Brilliant Red HE-3B dye onto *Bacillus* sp. immobilized in sodium alginate

T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
278	–5.628		
293	–4.948	–6.512	–4.004
321	–5.389		

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