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Biosorption of reactive dye from aqueous media using *Saccharomyces cerevisiae* biomass. Equilibrium and kinetic study

Research Article

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Abstract: The biosorption Brilliant Red HE-3B reactive dye by nonliving biomass, *Saccharomyces cerevisiae*, in batch procedure was investigated. Equilibrium experimental data were analyzed using Freundlich, Langmuir and Dubinin – Radushkevich isotherm models and obtained capacity about 104.167 mg g^{-1} at 20°C. The batch biosorption process followed the pseudo-second order kinetic model. The multi-linearity of the Weber-Morris plot suggests the presence of two main steps influencing the biosorption process: the intraparticle diffusion (pore diffusion), and the external mass transfer (film diffusion). The results obtained in batch experiments revealed that the biosorption of reactive dye by biomass is an endothermic physical-chemical process occurring mainly by electrostatic interaction between the positive charged surface of the biomass and the anionic dye molecules. The biosorption mechanism was confirmed by FT-IR spectroscopy and microscopy analysis

Keywords: *Saccharomyces cerevisiae biomass • Reactive dye • Biosorption • Equilibrium • Aqueous medium*

1. Introduction

The imperative demand of environmental quality assurance has led to the continuous diversification of analytical techniques, data interpretation and validation for the disposal of chemical compounds with ecological risks to the environment (air, water, soil). In this context, wastewater treatment is no longer a strict domain of a certain science, but it requires the approach of the matter in an interdisciplinary way (environmental chemistry, analytical chemistry, physical chemistry, ecology, ecotoxicology, electrochemistry, chemical technological process, biotechnology). Methods frequently applied in water depollution (precipitation, coagulation – flocculation, oxidation, reduction, ion exchange, membrane filtration, adsorption on charcoal or polymeric materials, electrochemical treatments, inverse osmosis, recuperation by evaporation, solvent extraction, *etc.*) are not efficient for total removal of toxic metal ions or organic matter [1,2]. These methods are characterized

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by incomplete removal of chemical pollutants, limited tolerance to pH change, moderate or no selectivity for metals, high reagents, materials and energy consumption, and production of toxic sludge or other by-products that also need treatment before disposal.

For the minimization of all these disadvantages, research has been focused toward techniques with special sensibility and selectivity, that are not subject to matrix effects, and permit the concomitant achievement of concentration and proper determination. These aspects have made possible the re-orientation of research to the application of different *biological procedures* for environmental protection. Promotion of the most advanced *bioprocesses* for minimization and even elimination of negative effects of pollutants is based on the main target of increasing the efficiency of depollution processes together with the consistent reduction of the cost for energy and manual labor, volume decreasing of manipulated raw materials, elimination of any pollution sources and no secondary production of dangerous wastes. The major advantage of bioprocesses, compared with certain physical-chemical treatments, is that more than 70% of organic matter, expressed by COD_{Cr}, may be converted into biosolids [3,4].

These bioprocesses include, among others, *biosorption* – the adsorption of some polluting chemical species onto natural or biological materials, having the role of an adsorbent material (*biosorbent*), which is still an open research topic for specialists in the field [5]. That is because the range of biosorbents is constantly widening, the types of polluting materials which can be inhibited by this technique are increasing in number, and there is also the aim to extend the applications of this technique in a continuous and dynamic technological flux, with a wide applicability on diverse types of matrices from the environment. *Biosorption* is characterized mainly by: low cost, elimination of ecological risk of the toxic compounds recovery and the possibility to treat large volumes of effluents with low concentrations of pollutants. Natural support, generated by plants, mushrooms, seaweed, microorganisms from soil or water is biodegradable and can be integrated in carbon cycles being also compatible with self control environmental processes. In line with these approaches, the depollution potential of different types of microorganisms opens new emerging biotechnological processes to be further studied and transformed into practical, industrial solutions.

Applied initially to remove inorganic species from industrial effluents [6-8], biosorption was expanded later to the removal of organic pollutant compounds, including dyes [9-12]. In the literature there are several studies on the use of yeasts and fungi (*i.e.*, *Aspergillus niger*, *Saccharomyces cerevisiae*, *Candida spp.*, *Rhizopus spp.*), for retaining different types of textile dyes (*i.e.*, Remazol Black B, Remazol Black 5, Reactive Red 3:1, Reactive Orange 13, Malachite Green, Methylen Blue, Congo Red *etc.*) [13-17].

Dyes represent an important organic pollutant of the aquatic medium with various negative consequences. Therefore, the discharge of dye-containing effluents into the water environment is undesirable, not only because of their color, but also as many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms, mainly because of carcinogens, such as benzidine, naphthalene and other aromatic compounds [4,5,18]. Without adequate treatment these dyes can remain in the environment for a long period of time. The environmental issues associated with residual dye content or residual color in treated textile effluents are always a concern for each textile operator that directly releases into the environment, including both sewage treatment works and commercial textile operations, in terms of respecting the color and residual dye requirements placed on treated effluent discharge [19]. Dye concentrations in watercourses higher than 1 mg L^{-1} caused by the direct discharges of textile effluents, treated or not, can give rise to public complaint. High concentrations of textile dyes in water bodies stop the re-oxygenation capacity of the receiving water and cut-off sunlight, thereby upsetting biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae [4,5].

In colored wastewater treatments have used various combined technologies, which consist of physical, chemical and/or biological technological steps. Of the most efficient procedures, the chemical oxidation, ion exchange, electrochemical reduction, ozonation, reverse osmosis, membrane technologies, photocatalytic degradation, biological processes, and adsorption are worth mentioning [19-22].

The main objective of this work is to investigate the biosorptive behavior of the non living biomass represented by *Saccharomyces cerevisiae* yeast for removal of the anionic reactive dye, Brilliant Red HE-3B from aqueous medium. The biosorption equilibrium, thermodynamic and kinetics were studied using different theoretical models in order to understand the process mechanism. FTIR spectroscopy has been used to characterize the biosorbent before and after loading the dye in order to obtain additional information about possible ways to bind the dye by the biosorbent.

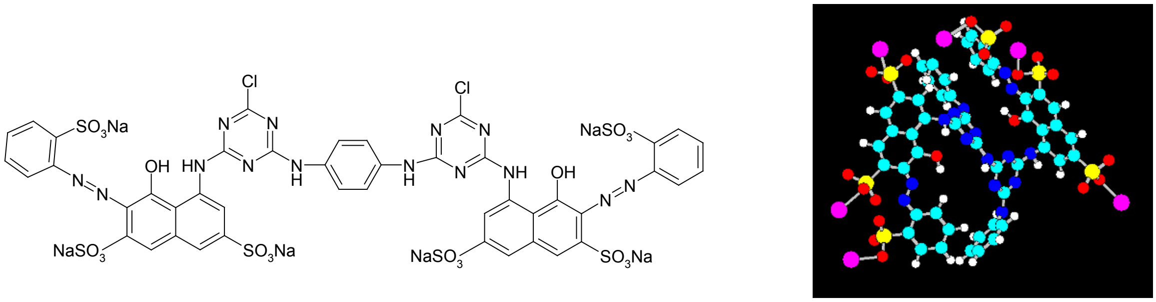

Figure 1. *Bis* (monochloro-*s*-triazine) reactive dye (Brilliant Red HE-3B, C.I. Reactive Red 120)

2. Experimental procedure

2.1. Materials

The experiments were carried out using as biosorbent a dead biomass represented by the yeast *Saccharomyces cerevisiae*, purchased from S.C. ROMPAK S.R.L (Baker's yeast) and prepared for work using a similar methodology presented in our previous paper,specifically a sample of yeast was inoculated over the growth medium (based on glucose solution and different inorganic salts) into a conical glass flask (1000 mL) equipped with a stirrer (200 rpm) for 48 hours of incubation at 30±1°C. After reaching this time, the biomass was harvested by means of centrifugation (MLW T23D centrifuge) at 6,000 rpm for 15 minutes, washed with distilled water, dried for 8 hours at 80°C and stored in a dry and light protected bottle until use [23].

Dye. 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. 1 was selected for this study. Stock solution (with 500 mg L^{-1} concentration) was prepared using the commercial salt with analytical reagent grade, form of dye and distilled water and the working solutions were obtained from stock solution by appropriate dilution with distilled water.

2.2. Batch biosorption equilibrium studies

The equilibrium biosorption studies were performed in 100 mL Erlenmeyer flasks by contacting amounts of 0.1 g of biomass (4 g L^{-1}) with 25 mL of dye solutions with different initial known concentrations (50 – 500 mg L^{-1}) and 2.3 pH values (adjusted with 1N HCl solution), at a constant desired temperature (thermostatic bath). It was conducted at three different temperatures (5, 20, 35°C) with a contact time of phases of about 6 hours. After reaching the equilibrium times the samples were centrifuged at 5,000 rpm for 10 min using a MLW T23D centrifuge and the dye content in supernatant was determined spectrophotometrically using a JK-VS-721N VIS Spectrophotometer at maximum dye wavelenght of 530 nm.

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 [5,24].

2.3. Thermodynamic of biosorption

The characteristic thermodynamic parameters were determined using known equations [25]:

$$\Delta G = -RT\ln K_L \quad (1)$$

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

where ΔG is Gibbs free energy (kJ mol^{-1}), ΔH is enthalpy (kJ mol^{-1}) and ΔS is biosorption entropy change (kJ $mol^{-1}K^{-1}$), R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the absolute temperature of solution (K) and KL is the values of Langmuir constant (L mol^{-1}).

2.4. Biosorption kinetic studies

The effect of contact time on the amount of dye sorbed onto biosorbent was determined in batch conditions where samples of 0.1 g biosorbent were added under stirring to 25 mL solution of dye with pH = 2.3 and initial concentration of 484 mg L^{-1}. The temperature was maintained at 20ºC with a thermostatic bath. At different times ranging from 10 to 360 min, samples of supernatant were taken and were analyzed, after centrifugation, by absorbance measurements in order to determine the dye solution content at time t. The extent of biosorption was expressed by the fractional attainment of equilibrium,

$$F = \frac{q_t}{q} \quad (3)$$

where q_t and q (mg g^{-1}) are the amounts of dye sorbed at time *t* and at equilibrium (6 h), respectively.

Table 1. The characteristics of the selected isotherm models.

Sorption isotherm model/ Assumption	Nonlinear / Linear form of equation	Isotherms parameters, significance
Freundlich **the surface heterogeneity and exponential distribution of active sites of the sorbent**	$q = K_F \cdot C^{1/n}$ $\lg q = \lg K_F + 1/n \lg C$	K_F and 1/n are constants related to the biosorption capacity and biosorption intensity (efficiency), respectively; a favorable sorption correspond to a value of $1<n<10$
Langmuir **- maximum adsorption corresponds to a monolayer of solute molecules on the sorbent surface, containing a finite number of energetically equivalent sites**	$q = \frac{K_L \cdot C \cdot q_0}{1+K_L \cdot C}$ $\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}$	q_0 is the maximum amount of sorbed solute (mg g^{-1}) and K_L is the constant related to the binding energy of solute (L mg^{-1}).
Dubinin-Radushkevich - suggests the nature of the sorption process – physical or chemical: E > 8 kJ mol^{-1} characterizes a physical sorption mechanism and values between 8 and 16 kJ mol^{-1} indicates an ion exchange mechanism	$q = q_D \exp(-B\varepsilon^2)$ $\ln q = \ln q_D - B\varepsilon^2$ $\varepsilon = RT\ln\left(1+\frac{1}{C}\right)$; $E = \frac{1}{\sqrt{-2B}}$	q_D is the maximum sorption capacity (mg g^{-1}); B is the activity coefficient related to mean sorption energy; ε is the the Polanyi potential and E – mean free energy of sorption (kJ mol^{-1})

Three of the most accepted kinetic models were applied in order to find the rate constant of biosorption process [26]: the pseudo – first order model (Lagergreen model), pseudo – second order model (Ho model) and intraparticle diffusion model (Webber and Morris model). The *pseudo-first order* kinetic model (Lagergreen model) based on sorption capacity (*q*) has the following general and linear forms:

$$\frac{dq_t}{dt} = k_1(q - q_t) \text{ and } \lg(q - q_t) = \lg q - \frac{k_1}{2.303}t \tag{4}$$

where: k_1 – rate constant of pseudo-first order model, (min^{-1}); q_t and q (mg g^{-1})- the amounts of dye sorbed at time t and at equilibrium (24 h), respectively.

The *pseudo-second order* kinetic model (Ho model), which assumes that the driving force of the process is the fraction of available sorption sites (q-q_t), has the general and linearized expressions:

$$\frac{dq_t}{dt} = k_2(q - q_t)^2 \text{ and } \frac{t}{q} = \frac{1}{k_2q^2} + \frac{1}{q}t \tag{5}$$

where: k_2 – rate constant of pseudo-second order model, g mg^{-1} min^{-1}; $k_2q^2 = h$ – initial sorption rate, mg g^{-1} min^{-1}. The *intraparticle diffusion model* (Webber-Morris model) is based on the affirmation that diffusion controls kinetics. The pore diffusion is the rate-limiting step if the plot q_t *vs.* $t^{1/2}$ is linear and passes through the origin. Their expression is:

$$q = k_d t^{1/2} + c \tag{6}$$

where: k_d- rate constant for intraparticle diffusion, mg g^{-1} $min^{-1/2}$; *c* – intercept to the y axis.

2.5. Analytical method

The biosorption capacity of the biomass was estimated using the amount of sorbed dye (q, mg of dye (g of biomass^{-1}), calculated as follows:

$$q = \frac{C_0 - C}{G} \cdot V \tag{7}$$

where C_0 and C are the initial and equilibrium (residual) concentration of dye in solution (mg L^{-1}), G is the amount of biomass (g) and V is the volume of solution (L).

2.6. Characterization of solid biosorbent

2.6.1. FT-IR analysis

For biomass characterization before and after biosorption of the reactive dye the FT- IR analysis was performed using a FT-IR BioRad spectrometer FTS2000 with 4 cm^{-1} resolution for 32 scans, using KBr pellets.

2.6.2. Microscopy analysis

Yeast cells were examined microscopically in slides, using a digital microscope Motic Image Plus 2.0 ML (Motic 1000) with X 40 objective. Microscopic preparations were made of yeast cells before and after biosorption. Also, we proceeded to the elution of adsorbed dye using as solvents: methanol, methanol - acetic acid (1: 1) and ethanol - acetone (3: 1). Then, samples (yeast cells and dye solution) were centrifuged at 6000 rpm (Centrifuge Boeco S-8) for 10 minutes, the supernatant was removed and the cells were subjected to a discoloring process for 30 minutes with the solvents mentioned above. After this step, the samples were centrifuged again at 6000 rpm and the cells were washed 3 times with distilled water, finally bringing it to the original volume of supernatant (10 mL). From each sample subjected to the process of discoloring process slides were prepared and examined microscopically.

2.7. Error analysis

Equilibrium biosorption data as well as the kinetic data were evaluated using different isotherms and kinetic models and the characteristic parameters were determined by linear regression analysis. In order to determine adequacy and accuracy of the models' equations with experimental data error analysis was carried out. Due to the inherent bias resulting from the linearization of isotherm and kinetic models, along with the linear regression coefficient R^2 (the determination coefficient), the degree of model fitness was evaluated using non-linear error functions; the Chi-square test, χ^2 [27] and the residual root mean square errors, RMSE [28]. The standard equations are as follows:

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(q_{e,exp} - q_{e,calc}\right)^2}{q_{e,calc}} \qquad (8)$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{N-2} \sum_{i=1}^{N} \frac{\left(q_{e,exp} - q_{e,calc}\right)^2}{q_{e,calc}}} \qquad (9)$$

where: $q_{e,}$exp and qe,calc represent the experimental and calculated values of sorption capacity (mg g^{-1}) and N is the number of experimental data.

Smaller values of RMSE and χ^2 and high values of correlation indicate the better model fitting and the better correlation between the experimental and calculated data with the model equation.

3. Results and discussion

3.1. Characterization of biomass before and after dye

3.1.1. FT-IR analysis

Infrared spectroscopy was used to estimate the main functional groups on the biomass surface before dye biosorption and also to appreciate their involving in the dye retention process, in order to obtain information about the biosorption mechanism.

The scientific literature mentions that the cell wall consists essentially of various organic compounds such as chitin, lipids, amino acids and other cellular components which can provide a means for the passive uptake of the dye. Among the main components are the mannoproteins and b – glucans (~85-90%), a smaller amount of chitin (1-3%) and lipids (2-3%) [29]. The variable proportion in which these components are present depends on the biomass source, the conditions of cultivation and growth method and also on the preliminary biomass preparation method as biosorptive material.

The FT-IR spectra were recorded for biomass before and after Brilliant Red HE-3B dye biosorption process and also for used dye and they are illustrated in Fig. 2. The spectra of the native (untreated) biomaterial as well as of the reactive dye BRed from Fig. 2 displayed many peaks reflecting the complex nature of the biosorbent and organic dye structure, respectively [29-32].

The FT-IR spectrum of *Saccharomyces cerevisiae* biomass (Fig. 2, line 1) reveals the presence of the numerous peaks assigned to the various *chemical compounds* (the peak at region about 1053.13-1074.35 cm^{-1} is the result of C-O stretching vibrations in polysaccharides; the peak about 1074.35 cm^{-1} is characteristic of the b (1→3) glucans, from 1053.13 cm^{-1} to the mannans, 1244.08 cm^{-1} is characteristic of nucleic acids, from the region 995-1073 cm^{-1} is assigned with the sugars and from the region of 1541.12-1647.21 cm^{-1} is characteristic of protein compounds, eventually due to stretching of secondary amide $RNHCOCH_3$ group) and to different *functional groups* which are able to interact with dye molecules. Among these highlights: the strong band at 3431.36 cm^{-1} assigned to O-H and N-H stretching vibrations (suggest the presence of hydroxyl and amine groups on the biomass surface, or secondary amide $RNHCOCH_3$ group of chitin component); 2924.08 cm^{-1} stretch in CH bonds in CH_3 and CH_2 groups; 1647.21 cm^{-1} is the result of C=O stretching vibrations; the peaks from the region 611–520 cm^{-1} offers indications about the existence of C-N-C stretching vibrations from protein structure.

In evaluating the FT-IR spectra of the biomass loaded with dye it can be observed that the intensity and position of peaks assigned to some characteristic functional groups (such as hydroxyl, amine, amide groups) from native biomass were either minimized or slightly shifted, suggesting that these functional groups can be involved in the dye molecules binding. After BRed dye biosorption the band at 3431.36 cm^{-1} (amide N-H stretching) shifted to 3442.93 cm^{-1}; 1074.35 cm^{-1}(overlapped with C-N stretching of the amino group) to 1076.28 cm^{-1}. Also, the appearance in the spectrum of red biomass of a characteristic peak of the sulphonic anion (1151.5 cm^{-1}) (characteristic for dye molecule – 1236.37 cm^{-1}) is noted.

All of these observations suggest that the dye biosorption mechanism may involve different electrostatic interactions between the positive charged

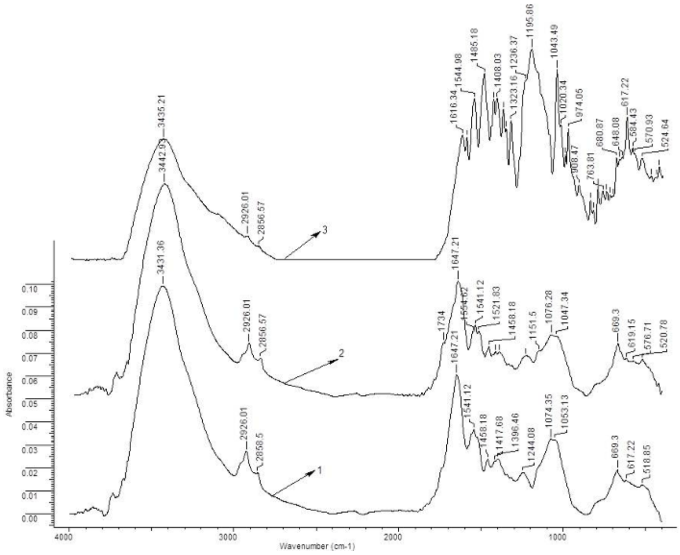

Figure 2. FT-IR spectra of *Saccharomyces cerevisiae* biomass (1), BRed - *Saccharomyces cerevisiae* biomass (2) and free BRed reactive dye (3) samples.

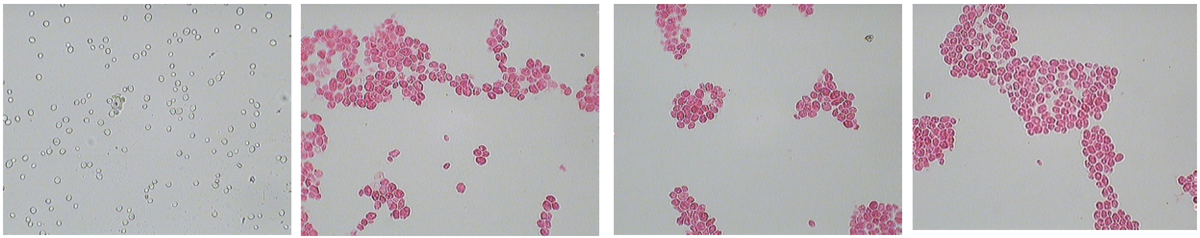
(a) (b) (c) (d)

Figure 3. Microscopy picture of native *Saccharomyces cerevisiae* biomass (a) and Bred - *Saccharomyces cerevisiae* biomass samples after methanol treatment (b), methanol- acetic acid mixture (c) and ethanol – acetone mixture (d).

surface of the biosorbent (as result of protonation of amine groups) and the anionic dye, as well as hydrogen bonding.

3.1.2. Microscopy analysis

The pictures of non-living native yeast sample (unloaded biomass) and dye treated sample (loaded biomass) are given in Fig. 3. The difference in the surface color of unloaded and loaded biomass's cell wall can be obviously observed by comparing images.

Similar results are reported in scientific literature. So, Aksu and Domnez [33] studying the biosorption of Remazol Blue by some strains of yeast, found the existence of an intracellular retention of the dye, in close relation with the yeast specie. Similar behavior was observed by all when they studied the biosorption of Remazol Turquoise Blue dye onto Candida utilis [34].

Microscopic images of native yeast and cells subjected to the discoloring process (Fig. 3) show the presence of dye in the cytoplasmic content of yeast cells even after solvent discoloration. The dye used not only penetrated the cells, but it bonded with intracytoplasmic structures of the cells, supporting the hypothesis of biosorption by chemical bonds.

3.2. Biosorption equilibrium

Our previous study [23] showed that achievement of a satisfactory sorption capacity is reached at pH 2.3 and biomass dose about 4 g L^{-1}, the two main factors influencing the process.

The equilibrium isotherm, defined as the amount of sorbate retained by the unit of sorbent (q, mg g^{-1}) as a function of the sorbate concentration at equilibrium in liquid phase (C, mg L^{-1}), represents an important instrument to study the biosorption process, in order to determine the characteristic quantitative parameters and to obtain initial information about the involved mechanism.

The biosorption isotherms of reactive dye Brilliant Red HE-3B on *Saccharomyces cerevisiae* biomass are presented in Fig. 4. The characteristics parameters of isotherms related to each sorption model (Freundlich,

Table 2. Characteristic isotherm parameters for biosorption of BRed dye onto *Saccharomyces cerevisiae*.

T, K	278	293	308
Freundlich isotherm			
K_F, (mg g^{-1})(L mg^{-1})$^{1/n}$	16.4305 ± 1.2954	21.158 ± 0.2915	34.9566 ± 1.2756
n	1.9495 ± 0.1404	1.9584 ± 0.03062	1.867 ± 0.1174
R^2	0.9799	0.999	0.9799
RMSE	4.9928	4.6567	11.5014
χ^2	1.4477	1.4212	5.9381
Langmuir isotherm			
q_o, mg g^{-1}	92.524 ± 11.247	103.68 ± 5.4975	157.729 ± 23.645
K_L, L mg^{-1}	0.1583 ± 0.035	0.1898 ± 0.0000795	0.248± 0.02032
R^2	0.9783	0.9945	0.9873
RMSE	5.7699	2.2725	2.3861
χ^2	2.0483	0.2991	0.3767
Dubinin – Radushkevich (DR)			
q_o, mg g^{-1}	189.308±13.021	188.897±6.583	295.379 ±37.014
B, mol^2 kJ^{-2}	0.00923±0.000423	0.00702±0.000176	0.00607±0.000403
E, kJ mol^{-1}	7.36±0,169	8,439 ± 0.106	9.076 ± 0.302
R^2	0.9917	0.9969	0.9826
RMSE	2.6499	2.1002	3.1589
χ^2	0.4977	0.3075	0.9138

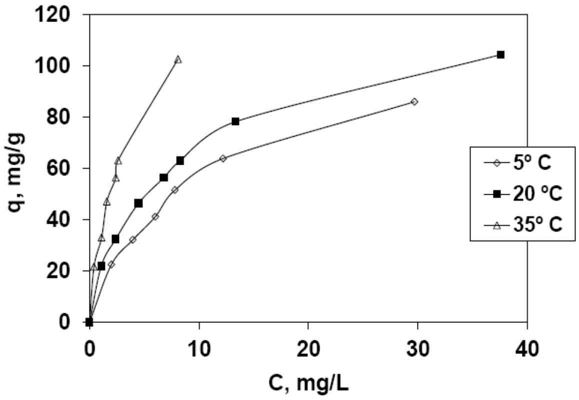

Figure 4. Biosorption isotherms of Brilliant Red HE-3B reactive dye onto *Saccharomyces cerevisiae* (biosorbent dose: 4 g L^{-1}; solution pH 2.3).

Langmuir and Dubinin – Radushkevich), calculated from the intercepts and slopes of the corresponding linear plots (figures not shown), together with their uncertainties (standard deviation) as well as the values of the correlation coefficients, R^2, the residual root mean square errors, RMSE and Chi-square test, χ^2, used to determine which model best describes the biosorption process of reactive dye Brilliant Red HE-3B onto *Saccharomyces cerevisiae* are presented in Table 2.

Analyzing the data from Table 2 the following conclusions can be highlighted:

- Evaluation of the values of the correlation coefficients, R^2, residual rot mean square error, RMSE, and Chi-square χ^2 - test values (Table 2) indicates that the experimental data of BRed dye biosorption onto *Saccharomyces cerevisiae* biomass were well fitted to both Freundlich and Langmuir models; however at increased temperatures the isotherms were more appropriate to the Langmuir model.

- The values of the Freundlich constant *n* are greater than unit, suggesting a favorable biosorption process.

- From the Langmuir model, an increase of the saturation capacity (monolayer coverage), q_o, with the increase of temperature can be observed, which reflects a better accessibility of biosorption sites. The value of biosorption capacity at a temperature of 20ºC has been found to be 104.167 mg dye (g of biomass)$^{-1}$, which is comparable with capacities reported in literature . Therefore, for the maximum biosorption capacity of some dyes retained onto biosorbents based on different types of biomass, the literature reports a wide range of values: 83.66 mg g^{-1} in the case of *Aspergillus parasiticus* as biosorbent for Reactive red 198 dye retained [35], 38.61.92 mg g^{-1} for Methylene Blue biosorbed onto *Cystoseira barbatula Kützing* [26],

Table 3. The thermodynamic parameters of the biosorption of Brilliant-Red HE-3B reactive dye onto *Saccharomyces cerevisiae* biomass.

T (K)	K_L (L mg^{-1})	K_L (L mol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
278	0.1583 ± 0.035	225009.4 ± 51.205	-28.4841 ± 0.0005	11.368 ± 1.123	143.2 ± 3.83
293	0.1898 ± 0.0000795	277677.4 ± 0.1163	-30.5333 ± 0.000001		
308	0.248± 0.02032	362824 ± 29.728	-32.7812± 0.0002		

Table 4. Kinetic parameters of Brilliant Red HE-3B biosorption by *Saccharomyces cerevisiae.*

Pseudo-first order kinetic model		Pseudo-second order kinetic model	
$q_{\text{experim}} =$ 92.62 mg g^{-1}			
Kinetic parameters	**Values**	**Kinetic parameters**	**Values**
		k_2, g mg^{-1} min^{-1}	0.000927 ± 0.00028
k_1, min^{-1}	0.0052 ± 0.0010	h, mg g^{-1}min^{-1}	7.8152 ± 2.381
$q_{\text{calculate}}$, mg g^{-1}	23.257 ± 3.672	$q_{\text{calculate}}$, mg g^{-1}	91.80 ± 2.277
R^2	0.8099	R^2	0.99615
RMSE	6.2082	*RMSE*	5.1234
χ^2	2.6877	χ^2	2.4251

23.7 and 14.99 mg g^{-1} in the case of live *Alternaria raphani* and autoclaved biomass of *Alternaria raphani* used for removal Reactive black 5 dye [36], respectively, 794.5 mg g^{-1} in the case of waste brewer`s yeast used for Acid Orange 7 biosorption [fost 27], and 11.32-26.37 and 8.83-19.74 mg g^{-1} for *Saccharomyces cerevisiae* biomass for sorbed Basic Blue 86 and Methylene Blue dye, respectively [37].

The values of the sorption energy obtained by the D-R equation, between 7.36 kJ mol^{-1} and 9.076 kJ mol^{-1} suggest that the biosorption process of the reactive dye occurs *via* a complex mechanism based on electrostatic attraction between the positive charged surface of the sorbent and the anionic dye, information confirmed by the FT-IR and microscopy analyses.

3.3. Thermodynamic parameters

The values of Δ*G* obtained from Eq. 1 and those of Δ*H* and Δ*S* from the slope and intercept of the plot of free energy change versus temperature (not presented) are given in Table 3.

The negative values of Δ*G* indicate the feasibility and spontaneity of the biosorption process. A decrease in the negative value of Δ*G* with the increase of temperature shows that the biosorption process is more favorable at higher temperature, probably due to the increased mobility of dye species in solution. However, temperature rises above 40 - 45ºC are not recommended because this starts the degradation of biomass, leading to an adverse effect on the sorption properties. The positive value of enthalpy change shows that the biosorption process is endothermic and the positive value of Δ*S* indicates affinity of the biomass towards the retained reactive dye and a high randomness at the solid-solution interface with some structural changes in the sorbate and the biosorbent. Also, the enthalpy value can offer some indication about the biosorption process nature: physical or chemical, based on the bonding strength between sorbate and biosorbent respectively. The literature indicates that a value in the range from 4 to 40 kJ mol^{-1} is characteristic of the physical biosorption process based on van der Waals interactions, hydrogen bonding, dipole–dipole and electrostatic interactions [38].

3.4. Biosorption kinetics

Processing the kinetic experimental data using different models is important for establishing the rate determining step, and to obtain additional information about the process mechanism. The kinetic parameters related to each model were calculated from the intercepts and slopes of the corresponding linear plots, and are presented in Table 4. The fitting of one or another model to the experimental data was conducted using the linear regression correlation coefficients, R^2, and also *RMSE* and χ^2 values.

The non-linearity of the plot lg $(q-q_t)$ *vs.* t (figure not shown), the small value of correlation coefficient (R^2 = 0.8099) and also high values of RMSE and chi-test (Table 4) indicate that the biosorption of BRed dye

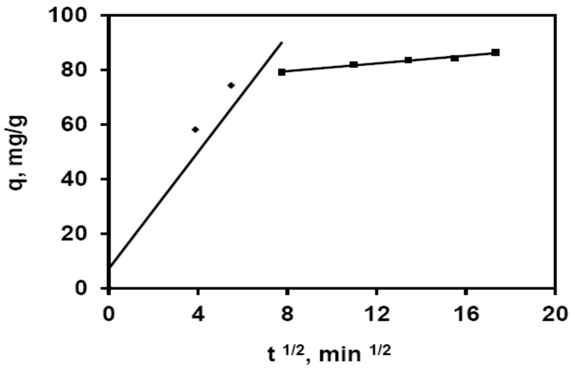

Figure 5. The applicability of the intraparticle diffusion kinetic models in the BRed dye biosorption onto *Saccharomyces cerevisiae* (C_0 = 484 mg L^{-1}; biosorbent dose= 4.0 g L^{-1}; pH = 2.3; temperature 20˚C).

onto *Saccharomyces cerevisiae* did not match well with the pseudo - first order kinetic model. Also, the values of $q_{experimental}$ and $q_{calculated}$ from the Lagergreen model differs appreciably, which reinforces the idea that BRed biosorption by considered biomass cannot be best described by pseudo-first order model.

The high value of correlation coefficient (R^2 =0.996) together with the smaller values of RMSE and chi-test and also, the good agreement between experimental and calculated *q* values, indicate the applicability of pseudo-second order kinetic model in predicting the kinetics of Brilliant Red HE-3B biosorption by *Saccharomyces cerevisiae*. Thus, the rate limiting step of the process may be the binding of BRed dye by active sites of the biosorbent surface. Similar behavior has been observed in retention of Methylene Blue by brown alga [26] or other unconventional sorbents such as wheat shells or rice husk [25,39].

The rate of dyes biosorption is, generally, governed by either liquid phase mass transport or the intraparticle mass transport. To get information about the diffusion mechanism, the kinetic data were processed based on the *intra-particle diffusion* (Weber-Morris) model. If the Weber-Morris plot (*q versus* $t^{1/2}$) is linear the intra-particle diffusion occurs and if the line passes through the origin, the intra-particle diffusion is the sole rate limiting step. The multi-linearity of the plots indicates the presence of two or more steps influencing the biosorption process [40,41].

The dependence on the amount of Brilliant Red HE-3B biosorbed by biomass versus $t^{1/2}$ (Fig. 5) reveals the presence of two line segments. The first steeper part (R^2 = 0.9164, k_{d1} = 10.685 ± 2.282 mg g^{-1} $min^{-0.5}$) is usually associated with external mass transfer (or instantaneous biosorption stage), while the second linear part (R^2 = 0.9789, k_{d1} = 0.707 ± 0.06 mg g^{-1} $min^{-0.5}$) indicates intraparticle diffusion into the porous structure of the biosorbent (gradual biosorption stage) [42]. These values show the presence of intraparticle diffusion (pore diffusion), but suggest that is not the only rate-limiting step of the biosorption. The intercept of the linear portions on the y-axis (*c* value) is a measure of the thickness of the boundary layer; the larger the value of c, the greater is the boundary effect.

4. Conclusions

The following conclusions are reached concerning the studied biosorption process of Brilliant Red HE-3B reactive dye onto *Saccharomyces cerevisiae* non-living biomass:

1. The equilibrium biosorption data fitted well to both Freundlich and Langmuir isotherm models. The obtained biosorption capacity was about 104.167 mg g^{-1} at 20 ^{0}C and increased with the increase of temperature suggesting an endothermic biosorption process. The values of the mean free energy of biosorption (*E*) obtained from the Dubinin - Radushkevich model between 7.372 and 9.054 kJ mol^{-1} suggest that biosorption of the dye occurs mainly *via* an ion-exchange mechanism based on electrostatic attraction between the positive charged surface of the biomass and the anionic dye.
2. The values of thermodynamic parameters confirm the feasibility and the endothermic behavior of the biosorption, suggesting the complex nature (physical-chemical) of the process.
3. The processing of the experimental data using different kinetic models (pseudo – first order, pseudo-second order and intra-particle diffusion models) indicates the applicability of the pseudo-second order model in predicting the kinetics of Brilliant Red HE-3B biosorption by *Saccharomyces cerevisiae* for the entire biosorption period. Thus, the rate limiting step of the process may be binding of BRed dye by active sites of the biosorbent surface. Also, the Weber-Morris plot (*q* versus $t^{1/2}$) indicates the presence of two main steps influencing the biosorption process: the intraparticle diffusion (pore diffusion), and the external mass transfer (film diffusion).
4. The obtained results of the present study give some valuable information about the possibility to use *Saccharomyces cerevisiae* non-living biomass as biosorbent to retain the Brilliant Red HE-3B reactive dye from acidic aqueous solutions and also, encourage the development of studies in order to bring the biomass into a form more easily manipulated during biosorption processes.

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