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# REMOVAL OF THE SYNTHETIC DYE REMAZOL BRILLIANT BLUE R FROM TEXTILE INDUSTRY WASTEWATERS BY BIOSORPTION ON THE MACROPHYTE *Salvinia natans*

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**Abstract** - Batch experiments were carried out for biosorption of Remazol Brilliant Blue R dye onto the macrophyte *Salvinia natans*. Effects of parameters such as initial dye concentration, pH, biosorbent dosage, contact time and temperature were investigated. Chemical and morphological characteristics of the biosorbent were evaluated before and after the biosorption process using methods such as Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TA), Differential Scanning Calorimetry (DSC) and Infrared Spectroscopy (FT-IR). Sorption kinetics were conducted and followed a pseudo-second order kinetic model. Equilibrium data were well represented by the Langmuir model. *Salvinia natans* exhibited a maximum uptake of 61.9 mg.g<sup>-1</sup>. The Dubinin-Radushkevich model indicated that the adsorption takes place by a physical process. Thermodynamic parameters were estimated. The negative values of the Gibbs energy indicated the spontaneous nature of the adsorption. The entropy was positive and the positive value of the enthalpy showed that the process is endothermic.

**Keywords:** Biosorption; Dye; Macrophyte; *Salvinia natans*.

## INTRODUCTION

Textile industries are responsible for producing large amounts of highly contaminated effluents by various types of synthetic dyes, which are characterized by being toxic and reactive. Textile effluents are ranked among the pollutants most harmful to the environment due to the high discharge volume and diversity in their composition, associated with the quantities of dye lost during the dyeing process (Al-Ghouti *et al.*, 2009). The dyes have environmental risks, especially to human health, due to their car-

cinogenic and mutagenic properties (Guaratini and Zanoni, 2000). Color affects the nature of water and inhibits sunlight penetration, reducing photosynthetic activity (Sivaraj *et al.*, 2001).

Considering this problem, there is a constant concern for the development of techniques able to remove pigmentation that has not adhered to the tissue fibers during the process steps, and is released together with the liquid waste of such industries (Araujo *et al.*, 2011; Souza *et al.*, 2011; Cerqueira *et al.*, 2009). Technologies of traditional wastewater treatment proved ineffective for the treatment of

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effluents containing synthetic textile dyes because of the chemical stability of these pollutants (Forgacs *et al.*, 2004). On the other hand, technologies such as adsorption have great efficiency in the treatment of industrial wastewater, mainly due to the high potential in removing organic matter and associated low cost (Bangash and Alam, 2009; Ncibi *et al.*, 2009).

Currently, one of the most widely used adsorbents is activated charcoal; however, its high cost is a disadvantage when used on a large scale (Schimmel *et al.*, 2010; McKay *et al.*, 1987; Low *et al.*, 1995). Many studies have been developed in order to seek low-cost adsorbents such as peat, ash, wood chips, silica, and clays (Silva *et al.*, 2010). The use of biomaterials as adsorbents for the treatment of wastewater is a potential alternative to conventional treatments (Vieira *et al.*, 2014; 2012; Mafra *et al.*, 2013; Pelosi *et al.*, 2013; Piccin *et al.*, 2011; Kumar *et al.*, 2005; Moreira *et al.*, 2001). However, these low cost adsorbents typically have low adsorption capacity (Srinivasan and Viraraghavan, 2010). Therefore, there is a huge demand for new materials such as aquatic plants, including macrophytes, which have adaptations that allow their growth in a vast region, from saturated soils to fully submerged in water. These kinds of plants are commonly associated with the purification capacity of water where they are present. They can act as biosorbents of conventional pollutants, heavy metals and organic compounds, and are persistent to pesticides (Iqbal and Saeed, 2007).

This paper proposes the use of the aquatic macrophyte *Salvinia natans* as biosorbent for the removal of Reactive Blue 19 dye, which is widely used in textile industries. Characterization of biomaterial and knowledge of the mechanisms involved, through the identification of the functional groups, in the biosorption process of dyes were determined by the following methods: Infrared Spectroscopy (FT-IR), Thermal Analysis (TG and DSC), Scanning Electron Microscopy (SEM) and Optical Microscopy. Biosorption assays were carried out for adsorption kinetics and equilibrium studies. The factors affecting the sorption process such as contact time, pH, initial dye concentration, biosorbent dosage and temperature were investigated. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models were adjusted to the experimental data. Kinetic models were evaluated in order to identify potential adsorption process mechanisms and to understand the possible physical-chemical interactions involved in adsorption phenomenon between the macrophyte surface and dye molecules.

## MATERIALS AND METHODS

### Preparation of Macrophyte and Dye Solutions

*Salvinia natans* biomass was collected by the CPAA (Research Center in Environmental Aquaculture) of the State University of Paraná – Brazil, crushed and sieved in to particles with average size of 0.75 mm for the adsorption tests.

Reactive Blue 19 dye (CI 61200, Remazol Brilliant Blue R,  $M_w$ : 626.54) was obtained from Sigma-Aldrich Co Ltd. The dye concentration values ranged from 20 to 300 mg.L<sup>-1</sup>. The control of solution Ph was done using HNO<sub>3</sub> (0.5 mol.L<sup>-1</sup>), and NH<sub>4</sub>OH (0.1 mol.L<sup>-1</sup>). Dye concentrations in solution were measured using a UV-vis spectrophotometer (Shimadzu, UVmini-1240) by monitoring the absorbance changes at the wavelength of 602 nm.

### Methods

#### Characterization of *Salvinia natans*

A morphological study of biomass was performed using methods such as Optical Microscopy (DMLM, Germany and Scanning Electron Microscopy (SEM) with the aim of obtain the structure of the material from surface images (Sputter Coater, BAL/TEC, SCD 050). FT-IR spectroscopy was used to identify the functional groups present in the macrophyte surface and the occurrence of chemical changes in the biomass after the biosorption process. Also Thermogravimetric and Differential Scanning Calorimetry analyses were used and allowed observing the behavior and thermal stability of materials before the adsorption step (Shimadzu, TGA-50).

#### Adsorption Kinetic Studies

Experiments were conducted in continuously stirred beakers containing 1500 ml of dye solution and 1.5 g of macrophyte with pH monitoring at room temperature. For the pH study the initial dye solutions (100 mg.L<sup>-1</sup>) were adjusted to pH 1.0, 2.0 and 3.0. The effect of initial concentration of dye was studied at pH 1.0. The values of concentration analyzed were 50, 100, 200 and 300 mg.L<sup>-1</sup>. Samples were withdrawn at predetermined intervals of time and were centrifuged at 3500 rpm for 10 min and the supernatant was analyzed. The amount of biosorbed dye per unit of macrophyte was calculated from the following equation:

$$q = \frac{(C_0 - C_f) \cdot V}{m} \quad (1)$$

where  $q$  is the dye uptake ( $\text{mg.g}^{-1}$ ),  $C_0$  and  $C_f$  are the initial and equilibrium concentrations of the dye ( $\text{mg.L}^{-1}$ ),  $V$  is the volume of solution (L), and  $m$  is the mass of biosorbent (g).

Kinetic data were described by pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1999) and intraparticle diffusion models (Weber and Morris, 1962). The model equations are represented as follows by Eq. (2), Eq. (3) and Eq. (4), respectively:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

$$q_t = k_{in}t^{1/2} + C \quad (4)$$

where  $q_e$  is the amount of dye retained in the solid surface at equilibrium ( $\text{mg.g}^{-1}$ ),  $q_t$  is the amount of dye retained at time  $t$  ( $\text{mg.g}^{-1}$ ),  $k_1$  corresponds to the reaction rate constant of pseudo-first order ( $\text{min}^{-1}$ ),  $k_2$  is the rate constant of reaction of pseudo-second order ( $\text{g.mg}^{-1}\text{min}^{-1}$ ),  $k_{in}$  is the mass transfer coefficient, which includes the effective diffusion, dimensions and physical characteristics of the particle ( $\text{mg.g}^{-1}(\text{min}^{1/2})^{-1}$ ) and  $C$  is a constant that gives an idea of the boundary layer thickness.

### Effect of Sorbent Loading

This study was conducted with 100 mL of RBBR solution ( $100 \text{ mg.L}^{-1}$ ) at room temperature and pH 1.0 for different concentrations of macrophyte (0.1 to  $5 \text{ mg.L}^{-1}$ ). When the biosorption achieved the equilibrium, samples were centrifuged at 3500 rpm for 10 min and the supernatant was analyzed.

### Adsorption Isotherms

Equilibrium experiments were carried out by contacting  $1 \text{ g.L}^{-1}$  of macrophyte with 100 mL of dye solution at different initial concentrations (20 to  $300 \text{ mg.L}^{-1}$ ). The samples were shaken (350 rpm) at four temperatures (15, 30, 40 and  $50 \text{ }^\circ\text{C}$ ). The dye concentration in solution before and after adsorption was determined by using a UV-vis spectrophotometer. The equilibrium data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models. The Langmuir isotherm is represented by the following equation:

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \quad (5)$$

where  $q_0$  represents the concentration of dye in the macrophyte for a total coverage of available sites ( $\text{mg.g}^{-1}$ ),  $b$  represents the Langmuir adsorption coefficient that represents the relationship between the rates of adsorption and desorption ( $\text{L.mg}^{-1}$ ) and  $C_e$  is the equilibrium concentration of dye in fluid phase ( $\text{mg.L}^{-1}$ ).

The essential characteristic of the Langmuir isotherm model can be expressed by the dimensionless constant called the equilibrium parameter ( $R_L$ ), given by Eq. (6):

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

where  $C_0$  is the initial concentration ( $\text{mg.L}^{-1}$ ) and  $b$  is the Langmuir constant ( $\text{L.mg}^{-1}$ ).

The Freundlich model isotherm is used to describe heterogeneous systems, and is given by:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where  $K_F$  is the Freundlich constant and indicates the adsorption capacity of the adsorbent ( $\text{mg.g}^{-1}$ ) and  $1/n$  is the heterogeneity factor.

The Dubinin-Radushkevich model can be expressed by the following equation:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (8)$$

where  $K_{DR}$  is the porosity factor ( $\text{mol}^2.\text{J}^{-2}$ ),  $q_m$  is the monomolecular adsorption capacity of dye biosorption by the biomass surface ( $\text{mg.g}^{-1}$ ) and the variable  $\varepsilon$  can be related to the equilibrium concentration ( $C_e$ ,  $\text{g.L}^{-1}$ ) as follows:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (9)$$

where  $\varepsilon$  is the Polanyi potential ( $\text{J.mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \times 10^{-3} \text{ kJ.K}^{-1}\text{mol}^{-1}$ ) and  $T$  is the absolute temperature.

A plot of  $\ln q_e$  versus  $\varepsilon^2$  ( $\text{J}^2.\text{mol}^{-2}$ ) yields a straight line, confirming the model. The mean free energy of adsorption  $E$  ( $\text{kJ.mol}^{-1}$ ) per molecule of the adsorbate when it is transferred from the solution to the biomass surface (Ergene *et al.*, 2009) can be calculated using the following equation:

$$E = (-2K_{DR})^{-1/2} \quad (10)$$

## Thermodynamic Parameters

The thermodynamic parameters for the adsorption process,  $\Delta H$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ),  $\Delta S$  ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $\Delta G$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ), were evaluated using Eq. (11) and Eq. (12):

$$\Delta G = -RT \ln(K_d) \quad (11)$$

$$\ln(K_d) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

where  $K_d$  is the adsorbate distribution coefficient ( $= q_{\text{eq}}/C_{\text{eq}}$  in  $\text{L}\cdot\text{g}^{-1}$ ).

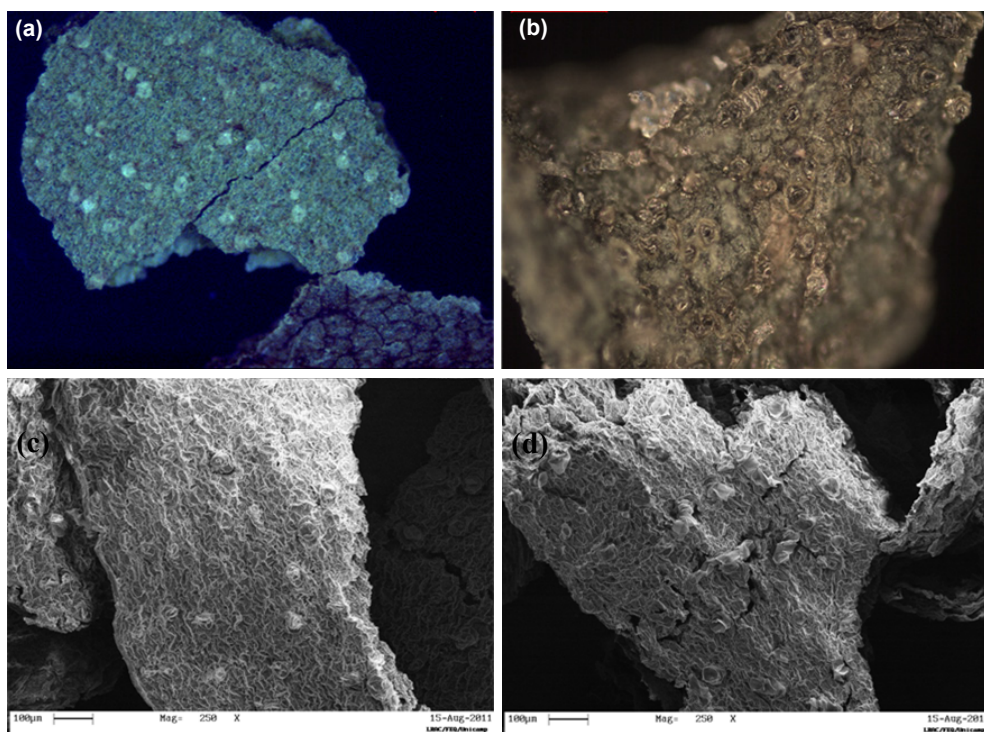
The plot of  $\ln(K_d)$  versus  $1/T$  must be linear with slope  $(-\Delta H/R)$  and intercept the y axis at  $(\Delta S/R)$ , providing the values for  $\Delta H$  and  $\Delta S$ . The variation in Gibbs free energy ( $\Delta G$ ) is the fundamental criterion of process spontaneity.

## RESULTS AND DISCUSSION

### Characterization of *Salvinia natans*

#### Surface Morphology

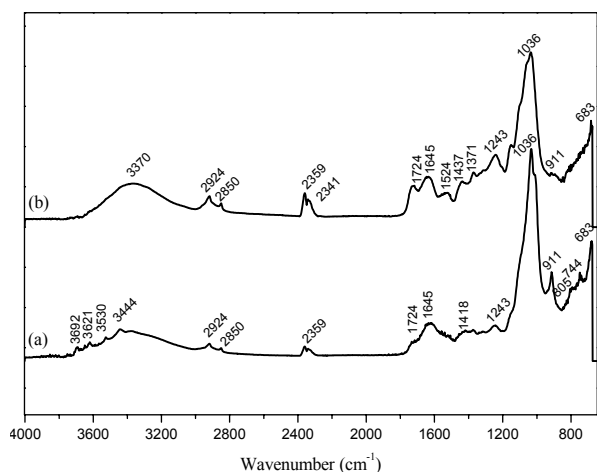
Figure 1 shows the micrographs obtained by OM and SEM analysis of macrophyte *Salvinia natans* before and after the biosorption process. In Figure 1-(a) there is a noticeable presence of salt crystals on the biomass surface, which can be attributed to the natural deposition of minerals. After biosorption (Figure 1-(b)), there was no change in the material surface. In Figure 1-(c),(d) it is possible observe the irregularity of the *S. natans* surface and the points assigned to crystalline salts. It can be seen that there was no significant structural changes in the macrophyte surface after the biosorption process, since the roughness remained approximately the same, and also the crystal structures.



**Figure 1:** OM micrographs (50x) of *S. natans* (a) "in natura" and (b) saturated with RBBR and SEM micrographs of *S. natans* (250x), (c) "in natura" and (d) saturated with RBBR.

## Functional Groups

Figure 2 shows the infrared spectrum obtained for biomass "in natura" and after the biosorption process. Through analysis of the bands and peaks present, it was possible to determine the main chemical bonds present in the samples, and determine the most prevalent organic functional groups. The bands at 2924-2850  $\text{cm}^{-1}$  are the asymmetric and symmetric stretch of methylene (H-C-H), respectively, the 1724  $\text{cm}^{-1}$  peak is stretching vibration of C=O. This peak was observed only in dye saturated biomass, as the 1524  $\text{cm}^{-1}$  band, which is that of secondary amide. The 1243  $\text{cm}^{-1}$  band is the C-O stretching of carboxylic acids, the 911  $\text{cm}^{-1}$  peak is the angular deformation of alkenes present only in the "in natura" biomass. The 900 - 690  $\text{cm}^{-1}$  peaks are due to aromatic compounds. The bands < 800  $\text{cm}^{-1}$  are in the fingerprint zone, which is also the region of phosphate and sulphur functional groups (Saygideger *et al.*, 2005). Some functional groups changed with biosorption. The FT-IR results showed that functional groups as carboxyl, alkenes and hydroxyl take part in dye binding.

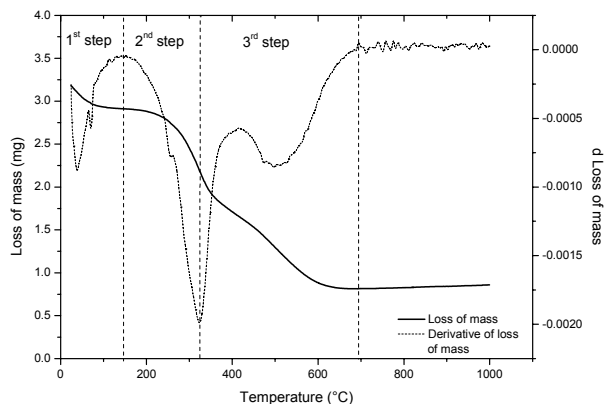


**Figure 2:** Infrared spectrum of *S. natans* (a) "in natura" and (b) saturated with RBBR.

## Thermal Analysis

Figure 3 shows the biomass thermogravimetric analysis (TA). The figure shows the plot of mass loss versus temperature and divides it into three steps, according to the main maxima and minima of the derivative curve. The occurrence of mass loss is mainly due to gases and vapor release, vaporization of liquids, dehydration, chemical decomposition and sublimation of solids (Chen and McKeever, 1997). The total mass loss of the macrophytes determined by TA was

72.94%. Table 1 shows the percentage of mass loss for each one of the three steps.

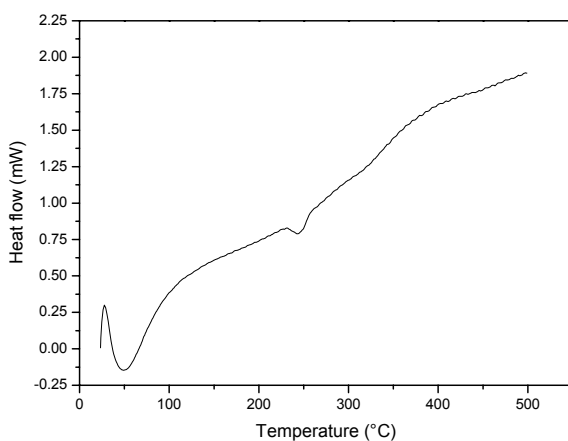


**Figure 3:** Thermogravimetric Analysis (TA) of *S. natans*.

**Table 1:** Loss of mass summary in different steps of TA.

Step	Temperature, °C	Loss of mass, %	Reason
1 <sup>st</sup>	25 - 150	8.57	Loss of water, microorganisms and organic matter
2 <sup>nd</sup>	150 - 325	24.52	Loss of hydroxyl
3 <sup>rd</sup>	325 - 700	60.79	Decarbonation

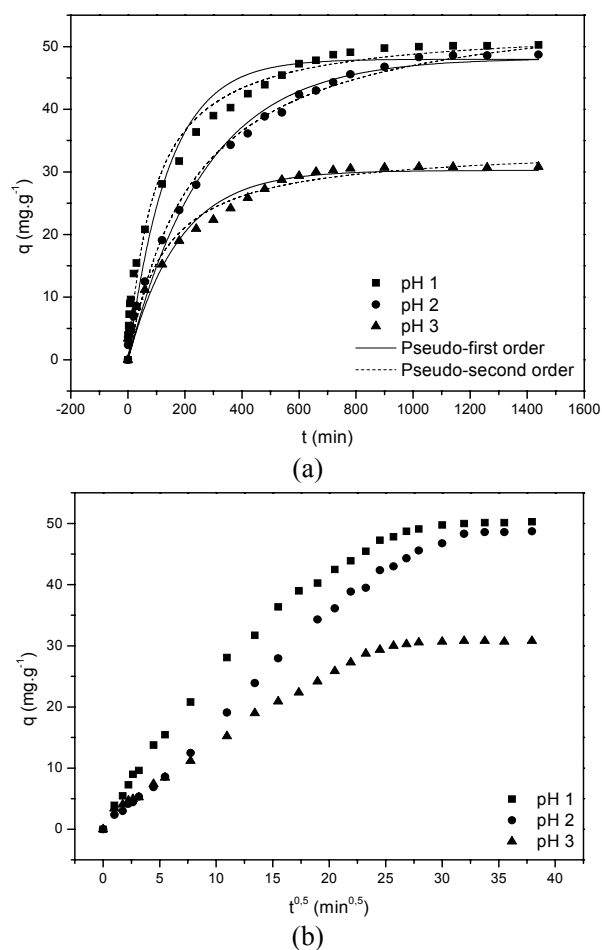
In Figure 4 is shown the Differential Scanning Calorimetry (DSC) curve of *Salvinia natans* biomass. It was observed that the macrophyte had two major endothermic events at temperatures of 50 °C and 160 °C. The first event is associated with the energy used to remove the biomass water of hydration molecules. The second event probably corresponds to the fusion energy of the macrophyte *S. natans*.



**Figure 4:** Differential Scanning Calorimetric (DSC) curve of *S. natans*.

## Effect of pH

The pH value of the solution exerts a profound influence on the adsorption process due to the impact that it causes on both surface binding-sites of the biosorbent and the ionization process of the dye molecules. In the present work, the effect of pH was studied for values between 1 and 3, as shown in Figure 5. It was observed that the equilibrium sorption capacity decreased with increasing pH from 1 to 3. The increase in biosorption of RBBR dye with decrease in solution pH was observed for other biomass (Aksu and Donmez, 2003; Aksu and Tezer, 2005; Iqbal and Saeed, 2007). The maximum amount of RBBR ( $50.2 \text{ mg.g}^{-1}$ ) was adsorbed at pH 1.0. This result can be explained by electrostatic forces. At lower pH, the surface of the macrophyte gets positively charged, which enhances the interaction of negatively charged dye anions with the surface of the macrophyte through the electrostatic forces of attraction (Won *et al.*, 2005).



**Figure 5:** Pseudo-first and second-order (a) and intraparticle diffusion (b) kinetic model fits for the pH effect on dye biosorption.

**Table 2:** The pseudo first-order, pseudo second-order and intraparticle diffusion kinetic constants obtained from the pH effect.

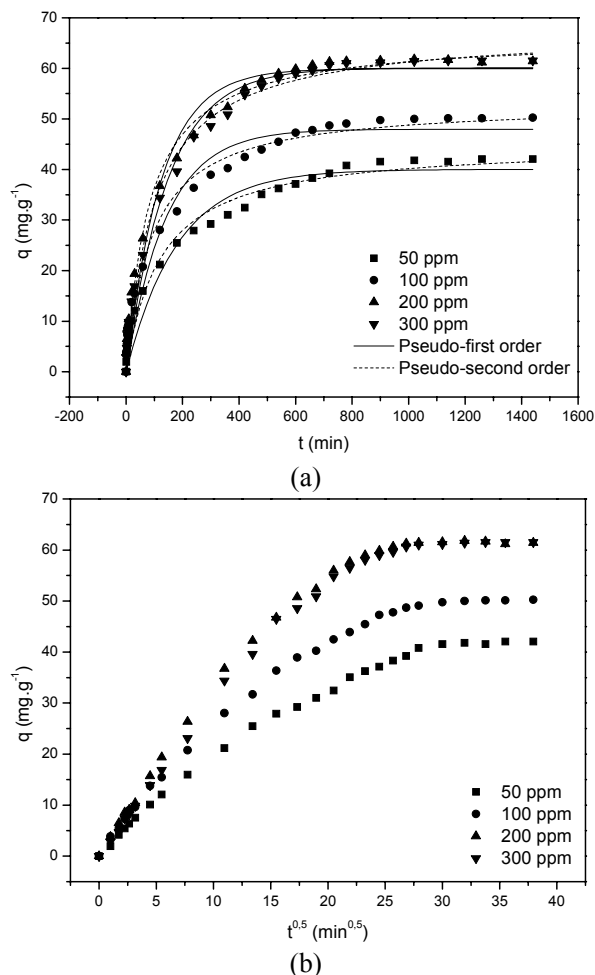
pH	Pseudo 1 <sup>st</sup> order			Pseudo 2 <sup>nd</sup> order		
	$q_1$ ( $\text{mg.g}^{-1}$ )	$k_1$ ( $\text{L.mg}^{-1}$ )	$R^2$	$q_2$ ( $\text{mg.g}^{-1}$ )	$k_2$ ( $\text{L.mg}^{-1}$ )	$R^2$
1	47.97	0.007	0.958	53.18	0.011	0.981
2	48.15	0.004	0.988	58.07	0.002	0.993
3	30.23	0.006	0.962	34.13	0.008	0.976
pH	Intraparticle diffusion					
	$k_{in}$ ( $\text{mg.g}^{-1}.\text{min}^{-1/2}$ )	C ( $\text{mg.g}^{-1}$ )	$R^2$			
1	1.25	1.52	0.993			
2	1.78	---	0.996			
3	2.21	2.37	0.992			

The correlation coefficients for the first order kinetic model were determined and compared with those of the second order kinetic model. Considering the study of the pH effect, the results presented in Table 2 show that the pseudo-second order model best fits the kinetic data. The plot of  $q$  versus  $t^{0.5}$  (Figure 5-(b)) gives a straight line that does not pass through the origin, showing that biosorption of RBBR by the macrophyte *Salvinia natans* is not an exclusivity of the intraparticle diffusion model. The  $K_{in}$  values were calculated by using correlation analysis (Table 2). The values of the intercept  $q$  give an idea about the boundary layer thickness; the larger the intercept, the greater the boundary layer effect will be (Kannan and Sudram, 2001). Similar results were found by Ergene *et al.* (2009) for biosorption of RBBR with heat-inactivated *Scenedesmus quadricauda*. The authors obtained a maximum capacity of  $47.9 \text{ mg.g}^{-1}$  at  $30^\circ\text{C}$  and pH 2.0 (Ergene *et al.*, 2009). The maximum RBBR biosorption capacity of *Salvinia natans* at equilibrium observed during the present study was also higher than values obtained in the literature. Polman and Breckenridge (1996) used the fungi biomass of *Botrytis cinerea* for removing dye and achieved maximum removal capacity of  $42 \text{ mg.g}^{-1}$ .

## Effect of Initial Dye Concentration and Contact Time

The effect of initial dye concentration on the biosorption was investigated between  $50$  and  $300 \text{ mg.L}^{-1}$  RBBR and an initial pH value of 1.0. The results are presented in Figure 6 and Table 3. Increasing the initial dye concentration increases the number of collisions between dye molecules and macrophyte. The amount of RBBR adsorbed increases from  $41.5$  to  $61.9 \text{ mg.g}^{-1}$  with an increase in initial dye concentration from  $50$  to  $300 \text{ mg.L}^{-1}$ . Table 3 shows the kinetic model parameters. The pseudo-second order

model also fits the experimental data better for all concentrations.



**Figure 6:** Study of biosorption variation with initial RBBR concentration. Pseudo-first and second order (a) and intraparticle diffusion (b).

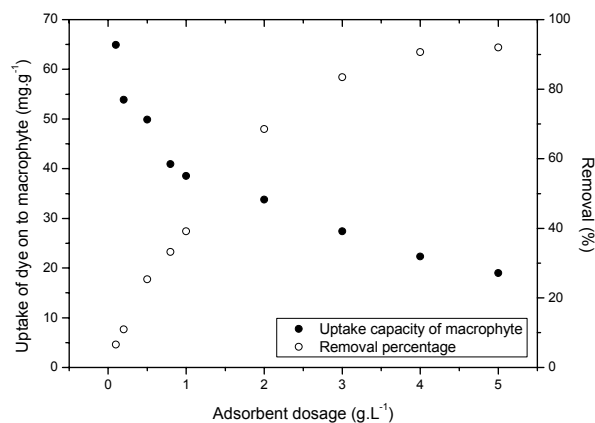
**Table 3:** The pseudo first-order, pseudo second-order and intraparticle diffusion kinetic constants obtained from the RBBR concentration effect.

Dye concentration (ppm)	Pseudo 1 <sup>st</sup> order			Pseudo 2 <sup>nd</sup> order		
	q <sub>1</sub> (mg.g <sup>-1</sup> )	k <sub>1</sub> (L.mg <sup>-1</sup> )	R <sup>2</sup>	q <sub>2</sub> (mg.g <sup>-1</sup> )	k <sub>2</sub> (L.mg <sup>-1</sup> )	R <sup>2</sup>
50	40.01	0.006	0.956	45.10	0.008	0.978
100	47.96	0.007	0.958	53.19	0.011	0.981
200	59.95	0.008	0.975	66.37	0.012	0.990
300	60.10	0.007	0.982	67.54	0.010	0.992
Dye concentration (ppm)	Intraparticle diffusion					
	k <sub>in</sub> (mg.g <sup>-1</sup> .min <sup>-1/2</sup> )	C (mg.g <sup>-1</sup> )	R <sup>2</sup>			
50	1.72	1.57	0.989			
100	2.21	2.37	0.992			
200	2.91	0.52	0.997			
300	2.97	1.65	0.994			

The values of  $q$  were found to be linearly correlated with values of  $t^{0.5}$ . Besides the linearity, intraparticle diffusion is not the main mechanism, meaning that others complex processes are taking place simultaneously. The equilibrium time necessary for adsorption was found to be 800 min for all initial dye concentrations, indicating that slow adsorption occurred and that the equilibrium reaching time is not dependent on initial dye concentration. Furthermore, the amount of RBBR adsorbed in 200 and 300 mg.L<sup>-1</sup> concentrations was approximately the same, indicating that this is the limit at which higher concentrations of dye does not mean a higher capacity for adsorption by the macrophytes.

### Effect of Sorbent Loading

The effect of biosorbent quantity on the removal of Remazol Brilliant Blue was investigated at 100 mg.L<sup>-1</sup> dye concentration. A range of concentrations from 0.1 to 5 g.L<sup>-1</sup> of *Salvinia natans* were mixed in the RBBR solution. From Figure 7 it is observed that the removal efficiency increased from 6.6 to 92% with an increase in the biosorbent loading from 0.1 to 5 g.L<sup>-1</sup>. This can be mostly attributed to an increase in the adsorptive surface area and the availability of more active adsorption sites. Furthermore, at higher biosorbent dosage, there is a very fast adsorption onto the biosorbent surface. However, with an increase in the biosorbent loading from 0.1 to 5 g.L<sup>-1</sup> the quantity of dye adsorbed per unit weight of macrophyte was reduced from 64.9 to 19.1 mg.g<sup>-1</sup>. A decrease in the  $q_e$  value with increasing biomass loading may be due to complex interactions of several factors such as availability of solute, interference between binding sites and electrostatic interactions (Aravindhan *et al.*, 2007). At higher biosorbent dosages, the available RBBR molecules are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low dye uptake.



**Figure 7:** Effect of initial *S. natans* dosage.



### Equilibrium Adsorption Studies

The adsorption equilibrium is reached when the amount of solute being adsorbed onto the adsorbent surface is equal to the amount being desorbed. When this occurs, the equilibrium solution concentration remains constant. Plotting solid phase concentration *versus* liquid phase concentration, it is possible to depict the equilibrium adsorption isotherm. Equilibrium data were analyzed using the Langmuir, Freundlich and Dubinin-Radushkevich equations. Figure 8 shows the Langmuir and Freundlich isotherms at four different temperatures. It is possible to see that the maximum adsorbed capacity is observed to increase as the process temperature rises, i.e., an increase in energy favors the adsorption on the macrophyte surface. This behavior indicates that this is an endothermic process.

The Langmuir isotherm theory is specific for monolayer adsorption, in which the biosorbent surface consists of sites equally available for adsorption and with equal energies of adsorption. According to the  $R_L$  parameter, Table 4, the isotherm can be con-

sidered favorable ( $0 < R_L < 1$ ) for dye biosorption. The Freundlich model is better applied to adsorption at heterogeneous sites on the biomass, with a non-established mechanism. Table 4 shows that the Langmuir isotherm model best fits the experimental data, indicating that the dye adsorption on the surface of the macrophyte takes place as a monolayer, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption (Aravindhana *et al.*, 2007). However, as seen from the  $R^2$  values, the Freundlich isotherm also fitted the experimental sorption data, and the  $1/n$  Freundlich constant values indicate that RBBR ions has high affinity for the biomass, because in all cases,  $1/n < 1$ , indicating favorable adsorption. The Dubinin-Radushkevich model determines if the adsorption occurred by a physical or chemical process. It is known that when the  $E$  value lies between 8 and 16  $\text{kJ}\cdot\text{mol}^{-1}$ , the adsorption process takes place by chemical ion exchange, while  $E < 8 \text{ kJ}\cdot\text{mol}^{-1}$  means that the adsorption process is physical (Argun *et al.*, 2007). As shown in Table 4, the  $E$  value for all temperatures is less than  $8 \text{ kJ}\cdot\text{mol}^{-1}$ , meaning that the adsorption of dye on the macrophyte surface is a physical process.

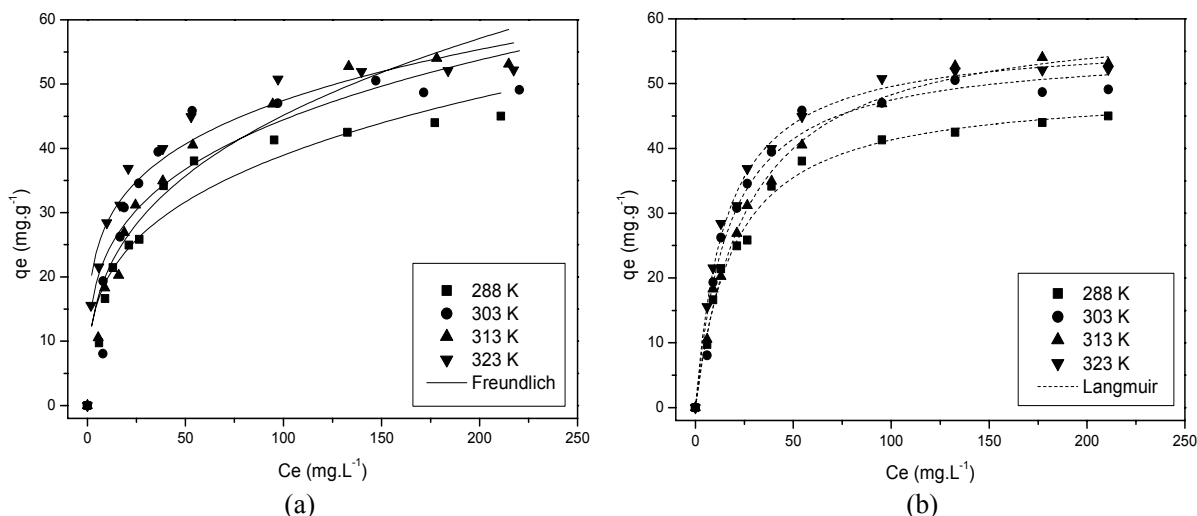


Figure 8: Langmuir (a) and Freundlich (b) isotherms for the adsorption at different temperatures.

Table 4: Langmuir, Freundlich and D-R isotherm model parameters.

Temp. (K)	Langmuir				Freundlich			Dubinin-Radushkevich		
	$q_e$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$b$ ( $\text{L}\cdot\text{mg}^{-1}$ )	$R^2$	$R_L$	$K_F$	$1/n$	$R^2$	$q_m$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$K_{DR}$ ( $10^{-5} \text{ mol}^2\cdot\text{J}^{-2}$ )	$E$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )
288	49.36	0.054	0.988	0.065	9.88	0.298	0.898	36.56	1.05	0.218
303	55.46	0.059	0.973	0.059	12.59	0.274	0.779	44.83	1.49	0.183
313	60.86	0.038	0.968	0.089	9.49	0.339	0.935	48.98	3.62	0.117
323	57.01	0.066	0.985	0.054	17.03	0.223	0.939	47.48	1.41	0.234

## Thermodynamic Parameters

The thermodynamic parameters such as change in standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption were determined and the results are given in Table 5. The  $\Delta G^\circ$  values increased in absolute value when the temperature increased, showing that the adsorption was more spontaneous at higher temperatures. The negative values of  $\Delta G^\circ$  indicate the degree of spontaneity of the adsorption process. The positive  $\Delta H^\circ$  value (32.0059 kJ.mol<sup>-1</sup>) characterizes an endothermic process and may be due to the removal of water molecules from the dye solution. This dehydration process requires energy and this process could supersede the energy released by the ions to attach to the surface of the biosorbent; this explains the endothermic behavior (Shah *et al.*, 2009). The positive value of the change in entropy ( $\Delta S^\circ$ ) reflects the increased randomness at the solid/solution interface during the adsorption of RBBR on the macrophyte surface.

**Table 5: Thermodynamic parameters.**

$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )			
		15 °C (288 K)	30 °C (303 K)	40 °C (313 K)	50 °C (323 K)
32.00	0.18	-20.24	-22.96	-24.78	-26.59

## CONCLUSION

The present work shows that the macrophyte *Salvinia natans* is an effective biosorbent for the removal of Remazol Brilliant Blue R from aqueous solutions. The amount of dye adsorbed varied with initial solution pH, dye concentration, biomass dosage, time of contact and temperature. With an increase in temperature, the amount of dye uptake increased, indicating that biosorption of RBBR onto *Salvinia natans* is an endothermic process. Furthermore, the biosorption process achieved better results under acid conditions due to electrostatic forces. At 40 °C, and pH 1.0, *Salvinia natans* exhibited a maximum uptake of 60.86 mg of RBBR per gram of macrophyte. The sorption data were found to follow pseudo-second order kinetics and equilibrium data fitted well to the Langmuir isotherm equation, ensuring a homogeneous biosorption process. The Dubinin-Radushkevich E value confirmed that the sorption takes place by a physical process. Thermodynamic parameters showed the spontaneity of the process and its endothermic character. The results

indicated that *Salvinia natans* is a promising low-cost technology bioadsorbent for the removal of waste dyes.

## NOMENCLATURE

$b$	Langmuir constant	L/g
$C_0$	initial concentration of dye in the fluid phase	
$E$	sorption energy	J/mol
$K_f$ and $n$	Freundlich coefficients	
$m$	mass of adsorbent	g
$q_{eq}$	concentration of dye in the solid phase	mg/g
$q_m$	maximum adsorbed capacity	mg/g
$q(t)$	concentration of dye in the solid phase	mg/g
$R$	ideal gas constant	
$T$	temperature	
$V$	volume solution	

## Greek Letters

$\beta$	Dubinin-Radushkevich constant
$\varepsilon$	Polanyi potential

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