



ASSESSMENT OF KINETICS, EQUILIBRIUM AND THERMODYNAMICS OF BLACK KROM KJR DYE ADSORPTION ONTO AQUATIC MACROPHYTE *Pistia stratiote*

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Abstract

The macrophyte *Pistia stratiote* was used as biosorbent for the removal of Black Krom KJR (BK-KJR) dye in synthetic aqueous solution. Initially, some tests were performed to verify the best operational conditions such as pH, biosorbent particle size, sorption temperature and stirring speed, which were later used in the kinetic and equilibrium tests. All tests were performed in duplicate. The highest removal rates of the pollutant were achieved at the process conditions of initial pH 2, granulometric mixture of roots, 30 °C and stirring speed of 80 rpm. In the kinetic test an equilibrium time of 24 h was found. The kinetic data were adjusted by applying the pseudo-first order, pseudo-second order and Elovich models, and as a result the best fit was found with the pseudo-second order model. In the equilibrium study it was found that, among the tested models, Langmuir model was the one that best fitted the experimental data, with a maximum sorption capacity (q_{max}) of $84.11 \pm 1.64 \text{ mg g}^{-1}$ and affinity constant (b) $0.025 \pm 0.001 \text{ mg L}^{-1}$. These results showed high potential of the macrophyte *Pistia* sp. as an alternative material to remove the BK-KJR dye.

Keywords: biosorption, dye, macrophyte, modeling, *Pistia stratiote*, thermodynamic parameters

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1. Introduction

With the rapid industrial development, high volumes of wastewater have been produced by industrial processes, and the release of such effluents, without a proper treatment, into environment has caused a rise of pollution levels. The water pollutants that affect biodiversity, ecosystem functioning and activities of natural aquatic systems comprise a variety of hazardous compounds (Roy et al., 2013). One of the major classes of pollutants are the dyes (Gupta and Suhas, 2009; Khambhaty et al., 2016), which are

widely used in textile, dyeing, pulp and paper, tannery, paint and printing, cosmetics, rubber, plastic, food and pharmaceutical products (Roy et al., 2013). Improper disposal (without treatment) of effluents containing these kinds of pollutant is of serious concern due to their adverse effects on many forms of life (Rafatullah et al., 2010), because besides causing aesthetic problems, they also decrease the photosynthetic activity in aquatic environments due to the reduction of light penetration. Moreover, many of the dyes are toxic, carcinogenic and harmful to human health (Módenes et al., 2015; Montazerozohori and

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Hoseinpour, 2017; Yang et al., 2011). In this sense, wastewater containing dyes must be carefully treated before releasing them into the natural water reserves.

Several types of treatment processes have been used in the removal of dye from wastewater, such as Advanced Oxidation Processes (AOP) (Kitinya et al., 2017; Ledakowicz et al., 2001; Módenes et al., 2012), chemical coagulation and flocculation (Verma et al., 2012), biochemical and chemical reduction (Ozkan-Yucel and Gokcay, 2017), photocatalysis (Gümüş and Akbal, 2011; Palácio et al., 2012), reverse osmosis and membranes (Kumar and Saravanan, 2011), adsorption (Fiorentin et al., 2010; Mittal et al., 2010; Scheufele et al., 2015), among others. Considering these techniques, the adsorption process is an attractive and effective treatment method (Sun et al., 2013), especially in terms of simplicity of design and operation and insensitivity to toxic substances (Monte-Blanco et al., 2017; Tanyildizi, 2011).

Activated carbon is the main used adsorbent due to its high sorption capacity (Tanyildizi, 2011). However, its high cost may jeopardize its practical application. Thus, alternative materials that are locally available, efficient and low cost are lately being investigated, such as agricultural solid waste (Salleh et al., 2011), pistachio hull waste (Moussavi and Khosravi, 2011), nonviable Penicillium (Yang et al., 2011), orange bagasse (Fiorentin et al., 2010), peanut hull (Tanyildizi, 2011), *Potamogeton crispus* (Gulnaz et al., 2011), fish scales (Ribeiro et al., 2015; Neves et al., 2017) and macrophytes (Barros and Silva, 2018; Pelosi et al., 2013; Saranya et al., 2011).

In this sense, the aim of this study was to evaluate the ability to remove BK-KJR dye from aqueous solution by using dried biomass of macrophytes *Pistia stratiote* as a biosorbent. To this end, preliminary tests were conducted to determine the effect of the particle size of biosorbent, initial pH of the solution, process temperature and stirring rate on dye removal. The best conditions obtained during the preliminary tests were later used in kinetic and equilibrium experiments. Pseudo-first order, pseudo-second order and Elovich kinetic models were used to fit the experimental data, while models of Langmuir, Freundlich, Sips and Redlich-Peterson were chosen to describe the equilibrium data.

2. Material and methods

2.1. Reagents

The dye used in the tests was the Black Krom KJR (Kromatica ®) (BK-KJR), obtained from a tannery industry located in the western region of Paraná, Brazil. For the aims of this study, a stock solution of 1000 mg L⁻¹ with distilled water was prepared and subsequently diluted for different tests as needed. The stock solution was stored in dark amber bottle. The pH of solutions was adjusted with HCl and NaOH 0.1 mol L⁻¹.

2.2. Biomass preparation

As biosorbent was used the macrophyte *Pistia stratiote*, commonly called water lettuce. The macrophyte was collected at the Institute for Research in Environmental Aquaculture (IREA) and dried by exposure to sunlight. Further the biomass was placed in a Cienlab drying oven at 40 °C in order to achieve the equilibrium moisture. The leaves were then separated from the roots of the plant, crushed in a knives-type grinder Willye model TE 648, and later separated by size with Tyler series vibrating sieves.

2.3. Determination of dye concentration

After each biosorption test, the concentration of BK-KJR dye was measured by UV spectrophotometer (Shimadzu UV-1800). Initially, the molecular absorption spectrophotometry measurements were carried out, in the wavelength range from 400 to 800 nm, with a 100 mg L⁻¹ dye solution. This experiment was performed to determine the wavelength in which the maximum absorption of light occurred.

After that, a standard curve was built, giving the absorbance as a function of dye concentration. For this purpose, some dilutions were made from the stock solution, in order to make 12 solutions with concentrations ranging between 1 and 100 mg L⁻¹.

2.4. Preliminary tests

Preliminary tests were made to evaluate the effect of the process parameters of DB-KJR dye removal by the macrophyte *Pistia stratiote*. The initial pH was studied in the range from 1 to 12. The adsorbent particle diameter was changed at the ranges from 0.850 to 0.500, 0.355 to 0.180, 0.150 to 0.106 mm; and mixture of sizes). The sorption temperature (T) was (20, 30 and 40 °C) and stirring speed (w) (40, 80 and 120 rpm).

In 125 mL Erlenmeyer flasks were placed 300 mg of adsorbent in contact with 50 mL of BK-KJR dye solution with initial concentration of 100 mg L⁻¹. The samples were placed in an orbital rotary shaker (TECNAL: TE-424) and remained there for 48 h under constant stirring velocity and temperature. After the experiment, the samples were withdrawn and centrifuged at 3000 rpm for 5 minutes in order to separate the solid and liquid phases, and an aliquot of the supernatant was taken for reading in the UV-Vis spectrum. The adsorbed amount of dye by macrophytes was calculated by the mass balance, according to Eq. (1).

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

where: q is the amount of dye adsorbed by biomass (mg g⁻¹); C_0 and C are the dye concentrations in the initial and final solution (mg L⁻¹), respectively; V is the solution volume (L); m is the mass of adsorbent (g).

2.5. Adsorption kinetics

For kinetic experiments, 300 mg of adsorbent in contact with 50 mL of dye solution with an initial concentration of 200 mg L⁻¹ and pH 2 were placed in 125 mL Erlenmeyer flasks. The samples remained, during the whole experiment, under agitation of 80 rpm and temperature of 30°C in an orbital rotary shaker (TECNAL: TE-424). At predetermined intervals of time (5 min to 60 h), the samples were taken out and centrifuged at 3000 rpm for 5 minutes and an aliquot of the supernatant was removed to determine the dye concentration with UV-Vis spectrum. The amount of dye adsorbed by the biomass of macrophyte *Pistia stratiote* was calculated by Eq. (1). The pseudo-first order model (or Lagergren model), pseudo-second order (or Ho model) and Elovich models were evaluated at the sorption kinetics description (see Table 1).

2.6. Adsorption isotherms

For the equilibrium study, 300 mg of adsorbent in contact with 50 mL of dye solution with different initial concentrations (from 25 to 900 mg L⁻¹) and pH 2, were placed in 125 mL Erlenmeyer flasks. Samples remained for 24 h under agitation of 80 rpm and 30°C in an orbital rotary shaker (TECNAL: TE-424). The samples were then withdrawn and centrifuged at 3000 rpm for 5 minutes and an aliquot of the supernatant was removed for reading it in the UV-Vis spectrometer.

The amount of dye adsorbed by macrophyte *Pistia stratiote* biomass was calculated by Eq. 1. Langmuir, Freundlich, Sips and Redlich-Peterson isotherms were used to fit the equilibrium experimental data (see Table 2). Both kinetic and equilibrium models' parameters were evaluated by

using the gradient method of Levenberg–Marquardt under the software Origin® 8.0.

2.7. Thermodynamic study

The thermodynamic parameters of the adsorption process, changes in Gibbs free energy (ΔG°), in enthalpy (ΔH°), and in entropy (ΔS°), were calculated using the experimental data at different temperatures. The Gibbs free energy was estimated by thermodynamic relation, according to Eq. (2) (Senthamarai et al., 2013).

$$\Delta G^\circ = -RT \ln(K_C) = -RT \ln\left(\frac{C_{ads}}{C_e}\right) \quad (2)$$

where: K_C is the adsorption equilibrium constant, C_e is the equilibrium dye concentration in solution (mg L⁻¹), C_{ads} is the amount of dye adsorbed per liter of solution (mg L⁻¹), R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature (K).

The dependence of ΔG° with enthalpy (ΔH°) and entropy (ΔS°) changes was determined the Eq. (3) (Scheufele et al., 2016), respectively by the intercept and slope.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

3. Results and discussions

3.1. Effect of the initial solution pH

An important influencing factor at dye adsorption has been referred to the solution pH. To find a suitable pH for the effective adsorption of DB-KJR by macrophyte *Pistia* sp., experiments were performed over a pH range from 1.0 up to 12.0 and the results are shown in Fig. 1.

Table 1. Kinetic models of adsorption

Model	Math Equation	Reference
Pseudo-first order	$q = q_e(1 - \exp(-k_1 t))$	Lagergren (1898)
Pseudo-second order	$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	Ho and McKay (1999)
Elovich	$q = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t$	Elovich and Zhabrova (1939)

where: k_1 and k_2 are the rate constants (h⁻¹) and (g mg⁻¹ h⁻¹), respectively; q_e and q are the amounts of dye adsorbed at the equilibrium and at a given time "t", respectively (mg g⁻¹); a is the adsorption rate (mg g⁻¹ h⁻¹) and b is the coefficient related with the extension of covered surface and activation energy of chemisorption (g mg⁻¹)

Table 2. Isotherm models of adsorption

Isotherm	Math equation	Application	Reference
Langmuir	$q_{eq} = q_{max} b C_{eq} / 1 + b C_{eq}$	Monolayer, homogeneous surfaces	Langmuir (1918)
Freundlich	$q_{eq} = K_F (C_{eq})^{1/n}$	Multilayer, heterogeneous surfaces	Freundlich (1906)
Sips	$q_{eq} = K_S (C_{eq})^{\beta_s} / 1 + a_s (C_{eq})^{\beta_s}$	Combination of Langmuir and Freundlich isotherms	Sips (1948)
Redlich–Peterson	$q_{eq} = K_{RP} C_{eq} / 1 + a_{RP} (C_{eq})^g$	Heterogeneous surfaces	Redlich and Peterson (1959)

where: q_{max} is the maximum adsorption capacity assuming a monolayer of the adsorbate (mg g⁻¹); b is the affinity constant (mg L⁻¹); C_{eq} is the concentration of adsorbate in solution at equilibrium (mg L⁻¹); K_F is the Freundlich constant (L g⁻¹); K_S (L g⁻¹) and a_s (L mg⁻¹) are Sips constants, respectively; K_{RP} (L g⁻¹) and a_{RP} (L mg⁻¹) are the parameters of Redlich-Peterson model; n , β_s and g are the exponents of Freundlich, Sips and Redlich-Peterson models, respectively

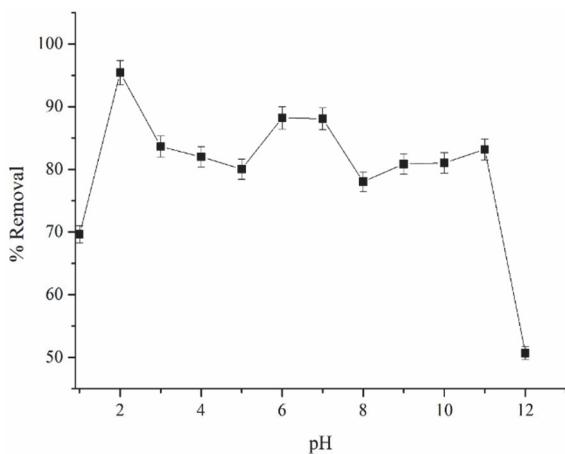


Fig. 1. Effect of initial solution pH on the removal of BK-KJR dye by biomass of *Pistia* sp. at the following process conditions ($T = 30^\circ\text{C}$, $w = 80$ rpm, $t = 96$ h, particle size mixture of roots, and $C_0 = 100 \text{ mg L}^{-1}$)

It can be noted, that the initial pH significantly affected the dye removal, which reached a maximum value of 95% at pH 2. Despite the higher removal rates of BK-KJR dye observed at pH 2, at neutral pH (6 and 7) and alkaline conditions (pH 11) the *Pistia* sp. biomass also showed BK-KJR dye adsorption capacity. This behavior may be related to the dye composition, which has sulphonate ($-\text{SO}_3\text{H}$) and amino groups ($-\text{NH}_2$) in its structure. These groups may be affected by the solution pH and can act like anionic or cationic sites (Errais et al., 2012). At acidic media sulphonate groups become negatively charged, interacting with functional groups at adsorbent surfaces (e.g. COOH, OH) which are protonated. On the other hand, at alkaline media amino groups become positively charged, interacting with other functional groups at adsorbent surface. In addition, other intermolecular forces, such as hydrogen bonds and Van der Waals forces may be related to the adsorption at neutral pH values (Ahmad and Kumar, 2012; Kiernan, 2001).

Furthermore, the observed decrease in the dye removal at the extreme acidic solution (pH 1) may be attributed to the biomass degradation. Due to the higher removal yields achieved at pH 2, this was the pH used for all subsequent tests. However, neutral and alkaline conditions could be used at the BK-KJR dye adsorption with the *Pistia stratiote* biomass depending on the pH values of the dye wastewater. During the experiments, no significant changes at pH solution were observed, in other words, the biomass did not alter the pH solution.

3.2. Effect of particle size

The particle size of the biosorbent is a process parameter which may influence the adsorption kinetics. It is known that the diffusional resistance to mass transfer increases at larger particle sizes. Thus, as the adsorption process is essentially considered as a surface phenomenon, the reduction of particle size can

allow faster removal process. Moreover, increasing the surface area due to smaller particle size reflects also in a bigger number of available sites, increasing indirectly the adsorption capacity (Tunç et al., 2009).

Table 3 shows the removal percentage of BK-KJR dye by macrophyte *Pistia* sp. on various ranges of particle diameter and the particle size mixture, which had a Sauter mean diameter of 0.261 mm. The particle sizes used at the sorption process were defined by the granulometric size distribution, based on the sizes that retained greater amounts of biomass. During the study, different parts of macrophyte were tested: (i) leaves, (ii) root (iii) and a mixture containing 50% leafs and 50% roots (root + leaf).

Table 3. Effect of particle diameter on the removal of BK-KJR dye by macrophyte *Pistia* sp. ($\text{pH} = 2$, $T = 30^\circ\text{C}$, $w = 80$ rpm, $t = 96$ hours, and $C_0 = 100 \text{ mg L}^{-1}$)

Particle diameter (mm)	% Removal		
	Leafs	Roots	Leafs + Roots
0.850–0.500	82 ± 4	93 ± 2	79 ± 4
0.355–0.180	88 ± 4	87 ± 2	84 ± 2
0.150–0.106	79 ± 4	89 ± 4	86 ± 3
Particles Mixture	80 ± 3	90 ± 3	81 ± 2

According to the results presented in Table 3, the use of macrophyte roots as biosorbent resulted at the highest percentage of dye removal when compared with the removal levels obtained by using leaves and the mixture of leaves and roots. However, the evaluation of the particle sizes in terms of dye removal by the macrophyte root resulted at similar rates values, confirmed by multiple mean comparison (Tukey's method). Considering the practicality of the biosorbent not-sieving, as well as the given results, the particle mixture of roots is the most appropriate, hence it was used for subsequent tests.

3.3. Effect of temperature

An increase in the temperature results in higher rates of dye molecules diffusion through the boundary layer and within the pores present in the adsorbent surface, due to the lower solution viscosity (Demirbaş and Alkan, 2013). In addition, at higher temperatures more dye molecules have sufficient energy to undergo an interaction with active sites of adsorbent and the dye mobility enhances to penetrate inside the adsorbent's pores (Ahmad and Rahman, 2011). Table 4 shows the percentage of BK-KJR dye removal by macrophyte *Pistia* sp. as a function of the adsorption temperature (20, 30 and 40 °C).

Analyzing the results presented in Table 4, the increase of the sorption temperature from 20 to 30 °C resulted in an increment of the dye removal rate by the biomass, changing the percentage values from 84 to 96%. However, the increase of the sorption temperature from 30 to 40 °C did not significantly change the removal percentage (97%) as it was evidenced by Tukey's test. Hence, for subsequent tests the temperature of 30 °C was chosen, in order to

minimize possible energy costs by the system's heating.

Table 4. Effect of temperature on the removal of BK-KJR dye by macrophyte *Pistia* sp. at the given operational conditions (pH = 2, w = 80 rpm, t = 96 hours; particle size mixture of roots, and $C_0 = 100 \text{ mg L}^{-1}$)

Temperature (°C)	% Removal
20	84 ± 2
30	96 ± 2
40	98 ± 2

Similar results were obtained by Moussavi and Khosravi (2011). They evaluated the effectiveness of pistachio hull powder for the elimination of dye methylene blue (MB) from contaminated streams and found that the increase of the solution temperature from 20 to 50 °C resulted in higher percentage levels of the equilibrium removal value of MB from 48 to 68%, under the selected experimental conditions (a solution with a concentration of 400 mg L⁻¹ dye). Ahmad and Rahman (2011), applied coffee husk based activated carbon (CHAC), prepared by physical-chemical activation for the removal of Remazol Brilliant Orange 3R (RBO3R) dye from aqueous solution. By investigating the effect of the temperature on the dye removal, they found a bigger adsorption capacity with an increase in the solution temperature from 303 to 333K. This result suggested that the adsorption process was endothermic. The estimated thermodynamic parameters of the adsorption process are presented in Table 5.

Table 5. Thermodynamic parameters calculated for the adsorption of BK-KJR dye onto macrophyte *Pistia* sp. biomass

$\Delta G^\circ /[\text{kJ mol}^{-1}]$	$\Delta H^\circ /[\text{kJ mol}^{-1}]$	$\Delta S^\circ /[\text{J mol}^{-1} \text{K}^{-1}]$
-4.053		
-8.366	82.92	
-10.017		298.20

The negative values of ΔG° indicated an spontaneous and favourable process (Ahmad and Kumar, 2012; Senthamarai et al., 2013), and the positive value of ΔH° confirms that the process is endothermic (Wu, 2007; Ahmad and Kumar, 2012; Çelekli et al., 2012; Dabbagh et al., 2018), as observed at the removal rates (Table 4). In addition, the elevated enthalpy change value ($\Delta H^\circ > 40 \text{ kJ mol}^{-1}$) suggests a chemisorption nature process (Çelekli et al., 2012), indicating that the process involves strong intermolecular forces (e.g. electrostatic interactions and hydrogen bond). Finally, the positive ΔS° indicated an increase in the randomness at the solid-solution interface (Wu, 2007; Zhang et al., 2013).

3.4. Effect of agitation speed

In order to evaluate the effect of stirring speed on the removal of BK-KJR dye by biomass of *Pistia* sp., three agitation speeds were tested: 40, 80 and 120

rpm. The results of the experiment are presented in Table 6.

Table 6. Effect of stirring speed on removal of the BK-KJR dye by macrophyte *Pistia* sp. under the following conditions (pH = 2; T = 30 °C; t = 96 hours; particle size mixture of roots, and $C_0 = 100 \text{ mg L}^{-1}$)

Stirring speed (rpm)	% Removal
40	91 ± 3
80	96 ± 3
120	95 ± 3

Evaluating Table 6, one can find out that an increasing of the stirring speed from 40 to 80 rpm resulted in an increase in the dye removal percentage from 91 to 96%, approximately. This can be explained by the fact that increasing the agitation speed reduces the film boundary layer surrounding the particles, thus increasing the external film transfer coefficient, and hence the adsorption capacity (Demirbaş and Alkan, 2013). However, increasing the stirring speed from 80 to 120 rpm resulted in no addition at the removal rate, which remained around 95%, suggesting that the speed of 80 rpm was sufficient to significantly reduce external diffusion resistance. Based on this fact, agitation speed in subsequent tests was maintained at 80 rpm.

3.5. Adsorption kinetics

The experimental data of the adsorption capacity (q) of BK-KJR dye by macrophyte *Pistia* sp. depending on the contact time is presented at Fig. 2, as well the simulation results describing the dynamics of adsorption kinetics.

According to the results presented in Fig. 2, it can be noted that during the first 4 h there was a rapid increase in the amount of adsorbed dye by reaching an adsorption capacity of approximately 26.8 mg of dye per gram of macrophyte. Furthermore, the necessary time for the system to reach equilibrium state was approximately 24 h, achieving $29.87 \pm 1.50 \text{ mg g}^{-1}$ (mg of dye per g macrophyte).

In order to study the mechanism of biosorption, several models, such as pseudo-first order (Lagergren), pseudo-second order (Ho) and Elovich model, were used to fit the obtained experimental data. In Table 7 are shown the estimated values of the models' parameters. From Table 7, the kinetic model that best fitted the data was the Pseudo-second order, according to the correlation coefficient (r^2), giving a value of q_e of $29.9 \pm 0.6 \text{ mg g}^{-1}$. This result suggests that the chemical adsorption controls the overall process. The adsorption process, therefore, involves valence forces as a result of sharing or exchanging electrons between the adsorbent and the adsorbate (Ho and McKay, 1999). This result is in accordance to the calculated thermodynamic parameters for the BK-KJR onto macrophyte *Pistia* sp. (Table 5), where enthalpy change values were characteristic of a chemisorption process ($\Delta H^\circ > 40 \text{ kJ mol}^{-1}$).

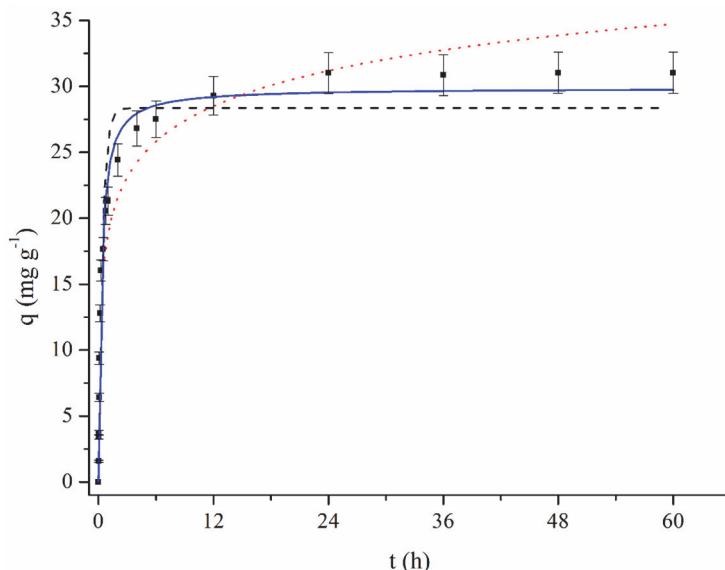


Fig. 2. Adsorption kinetics of BK-KJR dye by macrophyte *Pistia* sp. (Conditions: pH = 2, T = 30 °C, w = 80 rpm, particle size mixture of roots and C₀ = 200 mg L⁻¹) ■ Experimental data ——Pseudo-first order model; ---- Pseudo-second order model; •••• Elovich model

Table 7. Estimated parameter values of Lagergren, Ho and Elovich models fitted to experimental data of adsorption kinetics of BK-KJR dye by macrophyte *Pistia* sp.

Model	Parameters	Value of parameter
Pseudo-first order	k ₁ (h ⁻¹)	2.5 ± 0.4
	q _e (mg g ⁻¹)	28.4 ± 0.9
	r ²	0.9410
Pseudo-second order	k ₂ (g mg ⁻¹ h ⁻¹)	0.12 ± 0.01
	q _e (mg g ⁻¹)	29.9 ± 0.6
	r ²	0.9840
Elovich	a (mg g ⁻¹ h ⁻¹)	511 ± 131
	b (g mg ⁻¹)	0.26 ± 0.01
	r ²	0.9580

Similar results were achieved by Ahmad and Rahman (2011). In their experiments in order to reach the equilibrium state, times of approximately 22-24 h were necessary for the sorption process of Remazol Brilliant Orange 3R (RBO3R) dye by coffee husk based activated carbon. The studied initial dye concentrations varied from 100 to 250 mg L⁻¹. Furthermore, the authors used pseudo-second order model which fits well the kinetic data.

3.6. Equilibrium state of sorption process

The adsorption isotherms represent the equilibrium relationship between the amount of absorbed dye per unit of the biosorbent's mass (mg g⁻¹) and the dye concentration at a given temperature. They are fundamental for the description of how the adsorbate will interact with the adsorbent by showing the adsorption capacity of the adsorbent (Salleh et al., 2011).

However, to optimize the adsorption system design, it is important to establish a more appropriated correlation for the equilibrium curves (Arami et al.,

2008). For this end, Langmuir, Freundlich, Sips and Redlich-Peterson models were used to fit the equilibrium data. The estimated values of the models' parameters are shown in Table 8.

The simulation results with the evaluated models clearly showed that the Langmuir model was the one that best described the experimental data (see correlation coefficients (r²) shown in Table 8). The parameters values of this model were determined as follows: maximum adsorption capacity (q_{max}) of 84.11 ± 1.64 mg g⁻¹ and the affinity constant (b) equal to 0.025 ± 0.001 L mg⁻¹. Moreover, the Sips and Redlich-Peterson models were reduced to Langmuir isotherm, because the parameters β_S and g are equal to 1 (Foo and Hameed, 2010; Rangabhashiyam et al., 2014). This fact suggested, that the biosorption process created a monolayer coverage of the adsorbate at homogenous sites on the biosorbent surface.

The equilibrium data are plotted in Fig. 3 including the simulation data of Langmuir and Freundlich models. The simulation results obtained with the other models are not shown in the graph, since they were reduced to the form of Langmuir.

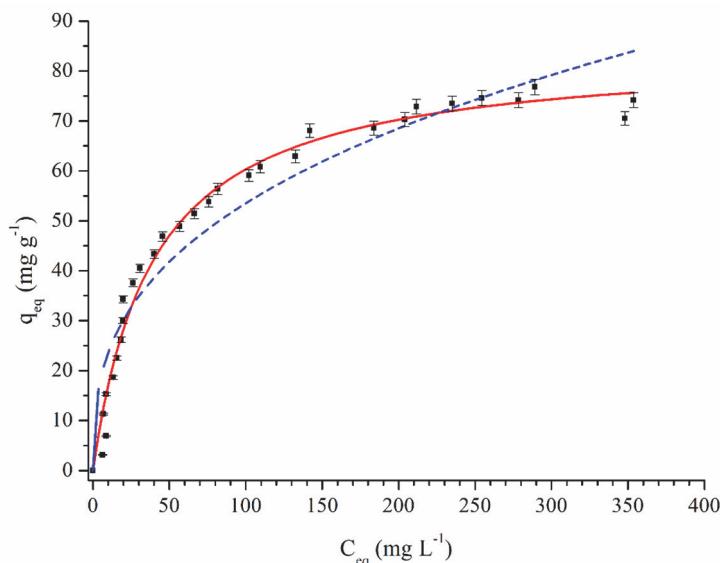


Fig. 3. Equilibrium data of the biosorption process of BK-KJR dye by macrophyte *Pistia* sp. and the simulation data of Langmuir and Freundlich isotherms (Conditions: pH = 2, T = 30 °C, w = 80 rpm, particle size mixture of roots, t = 24 hours)
■ Experimental data; — Langmuir model; - - - Freundlich model

Table 8. Isotherm parameters values estimated by the biosorption equilibrium data of the BK-KJR dye by macrophyte *Pistia* sp.

Isotherm	Parameters	Values of parameters
Langmuir	q_{max} (mg g ⁻¹)	84.11 ± 1.64
	b (L mg ⁻¹)	0.025 ± 0.001
	r^2	0.9832
Freundlich	K_F (L g ⁻¹)	10.35 ± 1.38
	n	2.80 ± 0.21
	r^2	0.9167
Sips	K_S (L g ⁻¹)	2.13 ± 0.11
	as (L mg ⁻¹)	0.020 ± 0.002
	β_S	1
Redlich-Peterson	r^2	0.9832
	K_{RP} (L g ⁻¹)	2.13 ± 0.19
	a_{RP} (L mg ⁻¹)	0.02 ± 0.01
	g	1
	r^2	0.9832

Módenes et al. (2013) used the macrophyte *E. crassipes* for the removal of reactive red dye BF-4B from solution with an initial concentration of 50 mg L⁻¹ and achieved a maximum sorption capacity equals to 20.38 ± 1.21 mg g⁻¹. Pelosi et al. (2013) used the *Salvinia natans* biomass for the removal of the dye Acid Orange 7. The equilibrium data was well represented by the Langmuir model, with a maximum adsorption capacity of 60.3 mg of dye per gram of macrophyte.

4. Conclusions

This study evaluated the possibility of using the macrophyte *Pistia stratiote* as a sorbent material. Highest percentages of dye removal were obtained by using a mixture of roots, initial pH 2, temperature of 30 °C and stirring speed of 80 rpm. The kinetic data showed a 24 h equilibrium time and were best represented by Ho's model. The equilibrium data were best described by the Langmuir isotherm, indicating

that the adsorption occurred on monolayer and homogeneous surfaces. The values of ΔG° , ΔH° and ΔS° suggested that the adsorption of BK-KJR dye onto macrophyte *Pistia stratiote* biomass is favorable, spontaneous, endothermic and it is a chemisorption process.

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