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Acid Orange 7 Dye Biosorption by *Salvinia natans* Biomass

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Textile industries are responsible for producing large amounts of highly contaminated effluents by several types of synthetic dyes, which are characterized by being toxic and reactive. Biosorption technique has been used as a promising treatment way to the pigments that do not adhere to the tissues fibers during dyeing process. Among the diversity of materials, macrophytes can act as biosorbents of conventional pollutants, heavy metals and organic compounds.

Batch experiments were carried out for biosorption of Acid Orange 7 dye onto macrophyte *Salvinia natans*. Effects of initial dye pH, contact time and temperature were investigated. Chemical and morphological characteristics of the biosorbent were evaluated before and after biosorption process using methods such as Scanning Electron Microscopy (SEM) and Infrared Spectroscopy (FT-IR).

Sorption kinetics was conducted and followed pseudo-second order kinetic model. Equilibrium data were well represented by Langmuir model. The *Salvinia natans* exhibited a maximum uptake of 60.3 mg of dye per gram of macrophyte. The results indicated that *Salvinia natans* is a promising low-cost technology bioadsorbent for the removal of waste dyes.

1. Introduction

Dye wastewater from textile industries is one of the most difficult industrial wastewaters to treat. One of the problems concerning the presence of color into waters is that it affects photosynthetic activity in aquatic life due to reduced light penetration. Moreover, synthetic dyes are harmful to human health as they have been shown to cause mutagenic effects as well as allergic dermatitis and skin irritation.

Many physical and chemical treatment methods including coagulation, adsorption, filtration and precipitation have been used for the removal of the dye from industrial wastewater. Unfortunately, these methods are not totally efficient, and the difficult in the treatment consists in the stability of these dyes, as they are kind of organic compounds that usually have a synthetic origin and complex molecular aromatic structures letting then difficult to be biodegraded (Hameed et al., 2007).

Among all treatment techniques, adsorption has been shown to be superior to the other techniques because of its simplicity of design, low cost and high efficiency. It also allows a potential biosorbent regeneration and high efficiency in detoxifying dilute liquid streams (Lima et al., 2011). Many studies have been developed in order to obtain low-cost adsorbents such as peat, ash, wood chips, silica, and clays (Vieira et al., 2011). However, these low cost absorbers typically have low adsorption capacity (Srinivasan and Viraraghavan, 2010). Therefore there is a huge demand for new materials such as aquatic plants including macrophytes. These kinds of plants are commonly associated with the purification capacity of water where they are present. This paper proposes the use of aquatic macrophyte *Salvinia natans* as biosorbent for the removal of Acid Orange 7 dye. Characterization of the biomaterial and identification of the functional groups were determined from the following methods: Scanning Electron Microscopy (SEM) and Infrared Spectroscopy (FT-IR). Parameters 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 experimental data. Kinetic models were evaluated in order to identify potential adsorption process mechanisms and to understand the possible physical-chemical interactions involved in the adsorption phenomenon of adsorption between the macrophyte surface and dye molecules.

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2. Materials and methods

2.1 Macrophyte and dye solution

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

Acid Orange 7 dye (CI 15510, Orange II Sodium Salt, M_W: 350.33), a synthetic dye, was obtained from Sigma-Aldrich Co Ltd. The dye solution was prepared by dissolving a weight amount of 1 g in 1 L of deionizer water. Then, were obtained concentration values ranged from 20 to 300 mg.L^{-1} used in the batch tests. The pH control of solutions was done using HNO_3 (0.5 mol.L^{-1}), and NH_4OH (0.1 mol.L^{-1}). Dye concentrations in solutions were measured using UV-vis spectrophotometer (Shimadzu, UVmini-1240) by monitoring the absorbance changes at the obtained maximum wavelength (λ_{max}) of 436 nm.

2.2 Characterization of *Salvinia natans*

A morphological study of the biomass was performed using Scanning Electron Microscopy (SEM) with the aim of obtaining the structure of material surface images (Sputter Coater, BAL/TEC, SCD 050).

FT-IR spectroscopy was used to identify the functional groups present in macrophyte surface and occurrence of chemical changes in biomass after biosorption process. Furthermore, the characterization of the biomass allows the knowledge of its properties influence in dye removing.

2.3 Adsorption kinetic studies

Experiments were conducted in continuously stirred beakers containing 1.5 L of dye solutions and 1.5 g of macrophyte with pH monitoring at room temperature. For the pH study the initial dye solutions (100 mg.L^{-1}) 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^{-1}. 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 according to the Eq. (1).

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

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

Kinetic data were described by pseudo-first order, pseudo-second order and intraparticle diffusion models. The equations are represented as follow Eq. (2), Eq. (3) and Eq. (4), respectively.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

$$q_t = k_{in} t^{1/2} + C \tag{5}$$

where q_e is the amount of dye retained in the solid surface at equilibrium (mg.g^{-1}), q_t is the amount of dye retained at time t (mg.g^{-1}), k_1 corresponds to the reaction rate constant of pseudo-first order (min^{-1}), K_2 is the rate constant of reaction of pseudo-second order (g.mg^{-1}min^{-1}), K_{in} is the mass transfer coefficient which includes effective diffusion, dimensions and physical characteristics of the particle (mg.g^{-1}(min$^{1/2}$)$^{-1}$) and C is the constant that gives an idea of boundary layer thickness.

2.4 Effect of sorbent loading

The effect of biomass concentration on the amount of color adsorbed was obtained by agitating erlenmeyer flasks with 100 mL of dye solution of 100 mg.L^{-1} concentration and pH fixed at 1.0 at room temperature. The macrophyte concentration was ranged from 0.1 to 5.0 g.L^{-1}. When the biosorption achieved the equilibrium, samples were collected and centrifuged at 3500 rpm for 10 min and the supernatant was analyzed.

2.5 Adsorption isotherms

Equilibrium experiments were carried out by contacting 0.1 g of macrophyte with 100 mL of dye solution in different initial concentrations (20 to 300 mg.L^{-1}). The samples were shaken (350 rpm) at four temperatures (15, 30, 40 and 50 °C). The dye concentration in solution before and after adsorption was determined using UV-vis spectrophotometer. The equilibrium data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models. Langmuir isotherm is represented by Eq. (6).

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \qquad (6)$$

where q_0 represents the concentration of dye in the macrophyte for a total coverage of available sites (mg.g^{-1}), b represents the Langmuir adsorption coefficient that represents the relationship between the rates of adsorption and desorption (L.mg^{-1}) and C_e is the equilibrium concentration of dye in fluid (mg.L^{-1}). Freundlich model isotherm is used to describe heterogeneous systems, and is given by Eq. (7).

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

where K_F is the Freundlich constant and indicates the adsorption capacity of the adsorbent (mg.g^{-1}) and $1/n$ is the heterogeneity factor.
Dubinin-Radushkevich model can be expressed by following Eq. (8).

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

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

$$\varepsilon = RT \ln\left(1 + {}^{1}/_{C_e}\right) \qquad (9)$$

where ε is the Polonyi potential (J.mol^{-1}), R is the universal gas constant (8.314×10^{-3} kJ.K^{-1}mol^{-1}) and T is the absolute temperature.
A plot of ln q_e *versus* ε^2 (J$^{2\cdot}$mol^{-2}) yields a straight line confirming the model. The mean free energy of adsorption E (kJ.mol^{-1}) per molecule of the adsorbate when it is transferred from the solution to the biomass surface can be calculated using Eq. (10).

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

3. Results and discussion

3.1 Surface morphology

Figure 1 shows the micrographs obtained by SEM analysis of macrophyte *Salvinia natans* before and after biosorption process. In Figure 1-a is possible to observe the irregularity of the *Salvinia natans* surface and a noticeable presence of salt crystals on the biomass surface, which can be attributed to the naturally deposition of minerals. In Figure 1-b shows that there was no significant structural changes in macrophyte surface after biosorption process, since the roughness remained approximately the same, and also the crystal structures.

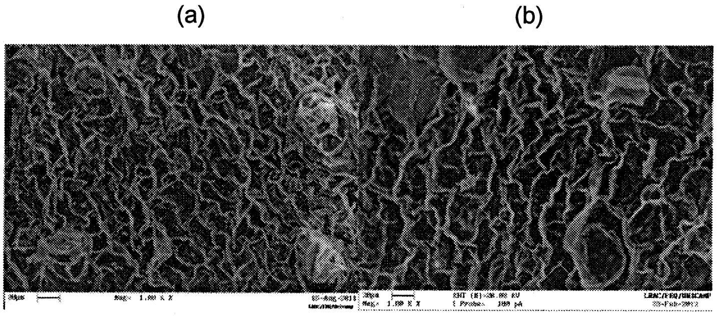

Figure 1: SEM micrographs of Salvinia natans (a) before and (b) after adsorption with Acid Orange 7 dye

3.2 Functional groups

It was possible to determine the main chemical bonds present in the samples, and determine the most prevalent organic groups. The band at 2924-2850 cm^{-1} is asymmetric and symmetric vibration of methylene ($C{=}H_2$), respectively, 1724 cm^{-1} peak is stretching vibration of C=O. This peak was observed only in dye saturated biomass, such as 1524 cm^{-1} band, which is of secondary amide. 1243 cm^{-1} band is the stretching C-O of carboxylic acids, 911 cm^{-1} peak is the angular deformation of alkenes present only in the biomass before dye contact. 900-690 cm^{-1} peaks are aromatic compounds. The FT-IR results showed that functional groups as carboxyl, alkenes and hydroxide take part of dye binding.

3.3 Effect of pH

The effect of pH was studied for values between 1 and 3 as shown in Figure 3. It was observed that the equilibrium sorption capacity decreased with increasing pH from 1 to 3. The increase in biosorption of dye with decrease in pH solution was observed for other biomass (Aksu and Tezer, 2005). The maximum amount of Acid Orange 7 (43.8 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 macrophyte through the electrostatic forces of attraction (Won et al., 2005).

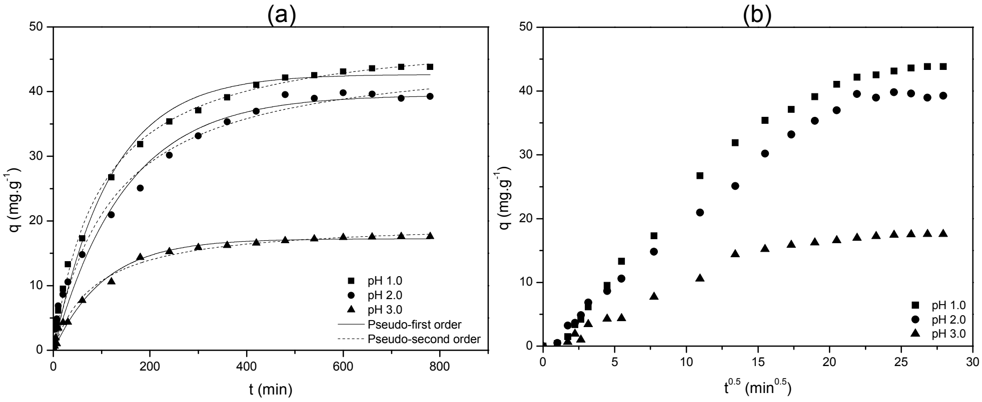

Figure 2: (a) Pseudo-first and second order and (b) intraparticle diffusion kinetic model fit. pH effect on dye biosorption

Table 1: The pseudo-first order, pseudo-second order and intraparticle diffusion kinetic constants obtained from pH effect and dye concentration studies

Acid Orange 7		Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
		q_1 (mg.g^{-1})	k_1 (L.mg^{-1})	R^2	q_2 (mg.g^{-1})	k_2 (L.mg^{-1})	R^2	k_{in}(mg.g^{-1}.min$^{-1/2}$)	c (mg.g^{-1})	R^2
pH study (pH)	1.0	42.6842	0.0084	0.9911	49.7975	0.0103	0.9978	1.0351	---	0.9284
	2.0	39.4909	0.0068	0.9823	46.7713	0.0082	0.9885	2.4843	---	0.9729
	3.0	17.2359	0.0095	0.9909	19.9347	0.0117	0.9934	2.0035	---	0.9844
Dye concentration study (mg.L^{-1})	50	24.3765	0.0181	0.9693	26.6408	0.0254	0.9901	1.5125	1.3779	0.9825
	100	42.6842	0.0084	0.9911	49.7957	0.0103	0.9979	2.4629	---	0.9935
	200	56.4089	0.0179	0.9832	61.8007	0.0245	0.9901	3.7225	1.8348	0.9783
	300	62.8305	0.0196	0.9766	68.5261	0.0268	0.9875	4.0999	2.8548	0.9658

The correlation coefficients for the first order kinetic model were determined and compared with that of second order kinetic model. Considering the study of pH effect, the results presented in Table 1, shows that pseudo-second order model best fits the kinetic data. The values of intercept q give an idea about the boundary layer thickness; it means that larger is the intercept grater boundary layer effect will be (Kannan and Sundram, 2001).

3.4 Effect of initial dye concentration and contact time

According to the kinetic parameters shown in Table 1, it is seen that pseudo-second order model fits better the experimental data for all concentrations. Figure 3-b shows that the values of q were found to be linearly correlated with values of t$^{0.5}$. Besides the linearity, the intraparticle diffusion is not the main mechanism meaning that other complex processes are taking place simultaneously.

The contact time between the adsorbate and adsorbent is an important parameter for designed adsorption process. In this study, the equilibrium time necessary for adsorption was found approximately 600 min for all initial dye concentrations, indicating that occurred slow adsorption and that the equilibrium reaching time is not dependent on initial dye concentration. Furthermore, the amount of dye adsorbed in 200 and

300 mg.L^{-1} concentrations was quite the same, showing that there is a limit in which higher concentrations of dye does not mean a higher capacity for adsorption by the macrophyte.

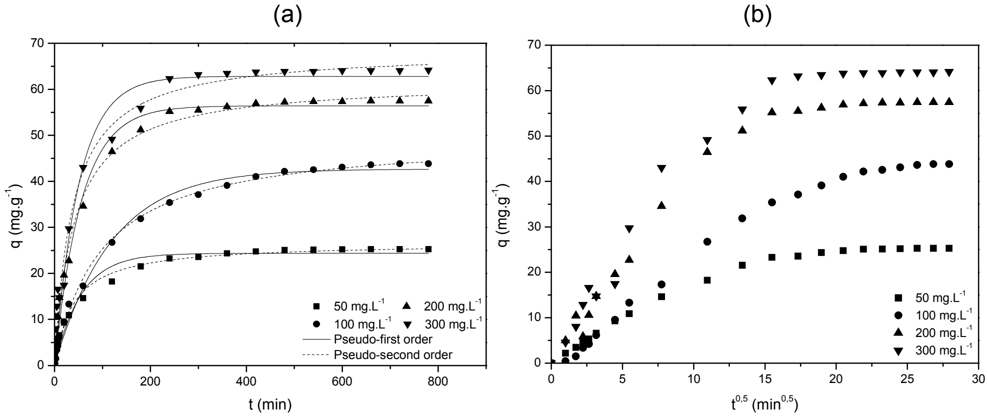

Figure 3: (a) Pseudo-first and second order and (b) intraparticle diffusion kinetic model fit. Initial dye concentration study

3.5 Effect of sorbent loading

The effect of biosorbent quantity on the removal of Acid Orange 7 was investigated at 100 mg.L^{-1} dye concentration. A range of concentrations from 0.1 to 5 g.L^{-1} of *Salvinia natans* were mixed in the dye solution.

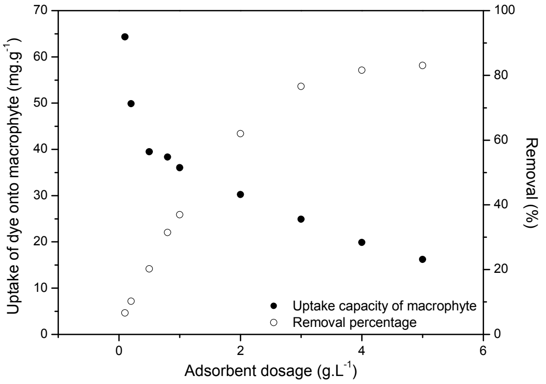

Figure 3: Effect of initial Salvinia natans dosage

From Figure 4 it is observed that removal efficiency increases from 6.6 to 83.2 % with increase in the biosorbent loading from 0.1 to 5 g.L^{-1}. 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 increase in the biosorbent loading from 0.1 to 5 g.L^{-1} the quantity of dye adsorbed per unit weight of macrophyte gets reduced from 64.4 to 16.5 mg.g^{-1}. A decrease in 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).

3.7 Equilibrium adsorption studies

Equilibrium data were analyzed using Langmuir, Freundlich and Dubinin-Radushkevich equations. Figure 4 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 macrophyte surface. According to R_L parameter the isotherm can be considered favorable ($0<R_L<1$) to dye biosorption. Table 2 shows that Langmuir isotherm model best fits the experimental data, indicating that the dye adsorption takes place by monolayer (Aravindhan et al., 2007). The Dubinin-Radushkevich model determines if the adsorption occurred by a physical or chemical process. It is known that when E < 8 kJ.mol^{-1} means that the adsorption process is physical (Argun et al., 2007). As shown in Table 2, the E value for all temperatures is less than 8 kJ.mol^{-1} meaning that the adsorption of dye on the macrophyte surface is a physical process.

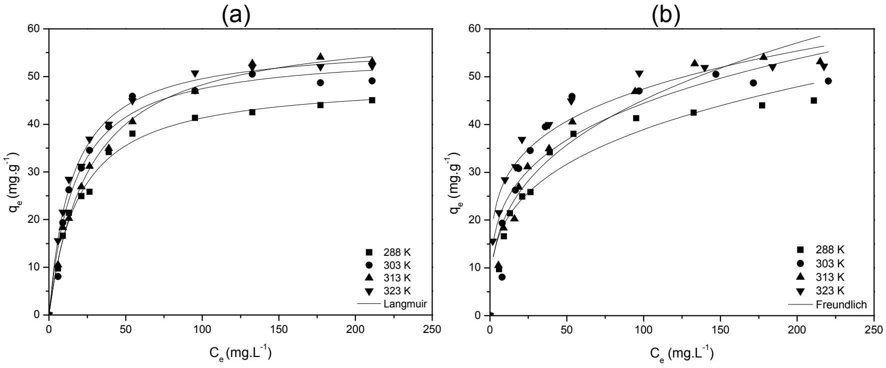

Figure 4: (a) Langmuir and (b) Freundlich isotherms fits for the adsorption at different temperatures

Table 2: Langmuir, Freundlich and D-R isotherms models parameters

Temp. (K)	Langmuir			Freundlich			Dubinin- Radushkevich		
	q_e (mg.g^{-1})	b (L.mg^{-1})	R^2	K_F	1/n	R^2	q_m (mg.g^{-1})	K_{DR} (10^{-5} mol^2.J^{-2})	E (kJ. mol^{-1})
288	46.5733	0.0454	0.9783	9.1861	0.2954	0.8477	34.5249	1.7002	0.1715
303	58.8178	0.0308	0.9655	7.9906	0.3535	0.8720	44.0128	3.4943	0.1196
313	69.5190	0.0243	0.9731	7.0637	0.4034	0.9183	47.5785	3.3510	0.1222
323	62.5284	0.0456	0.9844	10.8981	0.3227	0.9157	45.0728	3.4752	1.1995

4. Conclusions

The present work shows that the quantity of Acid Orange 7 dye adsorbed varied with initial solution pH, biomass dosage, dye concentration, time of contact and temperature. The biosorption process achieved better results under acid conditions. The sorption data were found to follow pseudo-second order kinetics and equilibrium data fitted by Langmuir model. The results indicated *Salvinia natans* constitutes a promising low-cost technology biosorbent for the removal of waste dyes.

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