



## Comparison of *Spirulina platensis* microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents

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### H I G H L I G H T S

- ▶ *Spirulina platensis* (SP) and activated carbon (AC) were used to remove RR-120 dye.
- ▶ The maximum adsorption capacities were found at pH 2 and 298 K.
- ▶ The values were 482.2 and 267.2 mg g<sup>-1</sup> for SP and AC, respectively.
- ▶ Adsorption was exothermic, spontaneous and favorable.
- ▶ SP and AC were effective to treat a simulated dye-house effluent.

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*Spirulina platensis* microalgae (SP) and commercial activated carbon (AC) were compared as adsorbents to remove Reactive Red 120 (RR-120) textile dye from aqueous effluents. The batch adsorption system was evaluated in relation to the initial pH, contact time, initial dye concentration and temperature. An alternative kinetic model (general order kinetic model) was compared with the traditional pseudo-first order and pseudo-second order kinetic models. The equilibrium data were fitted to the Langmuir, Freundlich and Liu isotherm models, and the thermodynamic parameters were also estimated. Finally, the adsorbents were employed to treat a simulated dye-house effluent. The general order kinetic model was more appropriate to explain RR-120 adsorption by SP and AC. The equilibrium data were best fitted to the Liu isotherm model. The maximum adsorption capacities of RR-120 dye were found at pH 2 and 298 K, and the values were 482.2 and 267.2 mg g<sup>-1</sup> for the SP and AC adsorbents, respectively. The thermodynamic study showed that the adsorption was exothermic, spontaneous and favourable. The SP and AC adsorbents presented good performance for the treatment of simulated industrial textile effluents, removing 94.4–99.0% and 93.6–97.7%, respectively, of the dye mixtures containing high saline concentrations.

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### 1. Introduction

Population growth increases the demand for industrial products. Dyes are used to colour the final products of different industries, such as textiles, paper and pulp mills, cosmetics, food, leather, rubber, etc. The generation of these products leads to the formation of wastewater contaminated with dyes. The textile industry is responsible for the use of 30% of synthetic dyes [1]. Of all dyed textile fibres, cotton occupies the number one position, and more than 50% of its production is dyed with reactive dyes [2]. It is estimated that about 10–60% of reactive dyes are lost during

textile dyeing, producing large amounts of coloured wastewater [1]. The dye-containing wastewater discharged from these industries can adversely affect the aquatic environment by impeding light penetration and, as a consequence, precluding the photosynthesis of aqueous flora [3,4]. Moreover, most of these dyes can cause allergy, dermatitis, skin irritation [5] and also provoke cancer [6] and mutation in humans [6,7]. It is rather difficult to treat reactive dye effluents because the complex aromatic molecular structure of these compounds. The molecular structures of reactive dyes make them more stable and biologically non-degradable [8–10]. Since global regulations have grown more stringent [1], the effluents of the textile industry have to be treated carefully before discharge [11,12]. This has resulted in increased demand for eco-friendly technologies to remove dyes from aqueous effluents [8,11,12].

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Adsorption is one of the most commonly employed methods for the removal of synthetic dyes from aqueous effluents [13,14], due its simplicity and high efficiency, as well as the availability of a wide range of adsorbents that can be applied [11–16]. This process transfers the dyes from the aqueous effluent to a solid phase, remarkably decreasing dye bioavailability to live organisms [11,12]. The decontaminated effluent can then be released to the environment or the water can be reutilised in the industrial process [15]. Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment [16]. Different kinds of adsorbents to remove dyes from aqueous solutions have been reported in the literature, such as agricultural wastes (cupuassu shell [3], aqai stalk [4], jujuba seeds [13], Brazilian pine fruit shell [15]), chemically modified lignin [16], chitosan [17], algae [18,19], inorganic silicates [20–22], activated carbons [12,23,24], carbon nanotubes [11,25,26] and others.

The blue-green algae *Spirulina platensis* is available in large quantities, as it is widely cultivated worldwide; its annual production is about 2000 tons [27,28]. Its biomass contains a variety of functional groups such as carboxyl, hydroxyl, sulphate, phosphate and other charged groups which can be mediate pollutant binding [29–31]. This microalgae has been successfully employed to remove heavy metals [28–30] and food dyes [31,32] from aqueous solutions. In spite of this, there are no studies currently available on the use of *S. platensis* biomass for the removal of textile dyes. In addition, it is important to compare *S. platensis* with commercial activated carbon (the main adsorbent used in dye removal [23]) in order to verify the potential of its application.

In this work, a comparison of the adsorbents *S. platensis* microalgae (SP) and commercial activated carbon (AC) for the removal of Reactive Red 120 textile dye (RR-120) from aqueous solutions was performed. This dye is widely used for textile dyeing in the Brazilian cloth industry. An alternative kinetic adsorption model was used to study the adsorption of the dye onto the SP and AC adsorbents. The equilibrium isotherms, determination of the thermodynamic parameters and utilisation of the adsorbents to treat a simulated dye-house effluent were performed for both adsorbents.

## 2. Material and methods

### 2.1. Solutions and reagents

The solutions were prepared with deionised water. Reactive Red 120 dye (RR-120) (C.I. 25810;  $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$ ,  $1469.98 \text{ g mol}^{-1}$ , see Supplementary Fig. 1) was obtained from Sigma–Aldrich (Switzerland) as a commercially available textile dye, with 80% dye content, and was used without further purification. RR-120 has six sulphonate groups. These groups present negative charges even in highly acidic solutions due to their  $pK_a$  values being lower than zero [24]. The main characteristic structural features of a typical reactive dye molecule are [33]:

- the reactive system, enabling the dye to form covalent bonds between the dye and the cotton fibre;
- the chromophoric group, contributing to the colour and much to the substantively for cellulose;
- a bridging group that links the reactive system to the chromophore;
- solubilising groups that make the dye soluble in water.

The stock solution ( $5.00 \text{ g L}^{-1}$ ) was prepared by dissolving the dye in deionised water. The working solutions were obtained by diluting the dye stock solution to the required concentrations. To adjust the pH of the solutions,  $0.50 \text{ mol L}^{-1}$  sodium hydroxide or

hydrochloric acid were used. The pH of the solutions was measured using a Schott Lab 850 set pH meter (Germany).

### 2.2. Adsorbents preparation and characterisation

In this research, *S. platensis* microalgae and commercial activated carbon were employed as adsorbents. The commercial activated carbon (Merck, Germany) with a particle size of  $<90 \mu\text{m}$  was used for comparison with *S. platensis*.

*S. platensis* (strain LEB-52) was cultivated in a 450L open outdoor photo-bioreactor, under uncontrolled conditions, in the south of Brazil. During these cultivations, water was supplemented with 20% Zarrouk synthetic medium [34]. At the end of cultivation, the biomass was recovered by filtration, washed with distilled water and pressed to recover the biomass with a moisture content of 76% (wet basis). The wet biomass (in cylindrical pellet form with a diameter of 3 mm) was dried in perforated trays using perpendicular air flow. The drying conditions were: air temperature  $60^\circ\text{C}$ , air velocity  $1.5 \text{ m s}^{-1}$ , relative humidity between 7% and 10% and load in the tray of  $4 \text{ kg m}^{-2}$  [35]. The dried biomass was ground by a mill (Wiley Mill Standard, No. 03, USA) and sieved until the discrete particle size ranged from 68 to  $75 \mu\text{m}$ . *S. platensis* was characterised according to the centesimal chemical composition [36] and energy dispersive X-ray spectroscopy (EDS) (Pioneer).

The SP and AC adsorbents were characterised by vibrational spectroscopy in the infrared region with Fourier transform (FTIR) using a Varian spectrometer, model 640-IR. The spectra were obtained with a resolution of  $4 \text{ cm}^{-1}$  with 100 cumulative scans. The surface analyses and porosity were carried out with a volumetric adsorption analyser (Nova 1000, Quantachrome Instruments) at 77 K. The samples were pre-treated at 473 K for 24 h under a nitrogen atmosphere in order to eliminate the moisture adsorbed on the solid sample surface. The samples were then submitted to 298 K in a vacuum, reaching a residual pressure of  $10^{-4} \text{ Pa}$ . For area and pore calculations, the multi-point BET and BJH [37] methods were used.

### 2.3. Adsorption studies

Batch contact adsorption experiments were carried out in order to evaluate the SP and AC adsorbents for the removal RR-120 dye from aqueous solutions. For these experiments, 50.0 mg of adsorbent were placed in 50 mL cylindrical polypropylene flasks containing 20.0 mL of the dye solutions ( $50.00\text{--}1200.0 \text{ mg L}^{-1}$ ), which were agitated for a suitable period of time ( $0.0833\text{--}6.00 \text{ h}$ ) using an acclimatised shaker at temperatures ranging from 298 to 323 K. The pH of the dye solutions ranged from 2.0 to 10.0. Subsequently, in order to separate the adsorbent from the aqueous solutions, the contents of the flasks were transferred to centrifuge tubes and then centrifuged at 10,000 rpm for 10 min. Aliquots of 1–10 mL of the supernatant were properly diluted with an aqueous solution fixed at pH 2.0.

The final dye concentration remaining in the liquid phase was determined by visible spectrophotometry at 534 nm. The adsorption capacity and the percentage dye removal were calculated by Eqs. (1) and (2), respectively:

$$q = \frac{(C_0 - C_f)}{X} \quad (1)$$

$$\% \text{Removal} = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

where  $q$  is the amount of dye adsorbed by the adsorbent ( $\text{mg g}^{-1}$ ),  $C_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ ),  $C_f$  is the dye concentration ( $\text{mg L}^{-1}$ ) after the batch adsorption procedure and  $X$  is the adsorbent dosage ( $\text{g L}^{-1}$ ).

The desorption experiments were carried out as follows: 50.0 mg L<sup>-1</sup> of RR-120 dye was shaken with 50.0 mg of either SP or AC for 1 h. Then, the loaded adsorbents were filtered through 0.2 μm cellulose acetate, then washed with water to remove the non-adsorbed dye. Then, the dye adsorbed on the adsorbents were agitated in 20.0 mL of an NaCl solution (0.05–0.50 mol L<sup>-1</sup>) an NaOH solution (0.05–0.50 mol L<sup>-1</sup>) or a mixture of NaCl (0.05–0.50 mol L<sup>-1</sup>) + 0.10 mol L<sup>-1</sup> NaOH for 15–60 min. The desorbed dye was separated and quantified as described above.

#### 2.4. Kinetic adsorption models

Please see the Supplementary material [38–41].

#### 2.5. Equilibrium models

Please see the Supplementary material [42–44].

#### 2.6. Quality assurance and statistical evaluation of the kinetic and isotherm parameters

Please see the Supplementary material [45–49].

#### 2.7. Simulated dye-house effluent

Two synthetic dye-house effluents containing four representative reactive dyes and one direct dye used for colouring fibres and their corresponding auxiliary chemicals were prepared at pH 2.0, using a mixture of different dyes most often applied in the textile fibre industry. According to the practical information obtained from a dye-house, typically 10–50% [1] of reactive dyes and 100% of the dye bath auxiliaries remain in the spent dye bath, and its composition undergoes a 5–30-fold dilution during the subsequent washing and rinsing stages [11,50]. The concentrations of the dyes and auxiliary chemicals selected to imitate an exhausted dye bath are given in Supplementary Table 1.

### 3. Results and discussion

#### 3.1. *S. platensis* and commercial activated carbon characterisation

The FTIR spectrum of *S. platensis* (Fig. 1A) shows O–H bond stretching mixed with the NH<sub>2</sub> group at 3370 cm<sup>-1</sup> (intense and broad band) [12,24]. The bands at 2920 and 2859 cm<sup>-1</sup> are related to asymmetric and symmetric stretching of CH<sub>2</sub> groups, respectively [12,24]. Scissor bending of the NH<sub>2</sub> group can be observed at 1659 and 1535 cm<sup>-1</sup> (sharp and intense bands) [27,30]. The bands at 1224, 1149, 1021 cm<sup>-1</sup> can be assigned to the C–N stretch of amide or amine groups [28,31]. The adsorption bands in the region 750–900 cm<sup>-1</sup> can be attributed to P–O, S–O and aromatic C–H stretching vibrations [28]. Fig. 1B shows the FTIR vibrational spectra of the commercial activated carbon. The intense absorption band at 3437 cm<sup>-1</sup> is assigned to O–H bond stretching [12,24]. The two CH<sub>2</sub> stretching bands at 2924 and 2854 cm<sup>-1</sup> are assigned to asymmetric and symmetric stretching of CH<sub>2</sub> groups [12,24]. The sharp band at 1736 cm<sup>-1</sup> is assigned to the carbonyl group of carboxylic acid [12]. The sharp intense peak observed at 1631 cm<sup>-1</sup> is assigned to aromatic C=C ring stretching [12,24]. In addition, there are several small bands and shoulders in the range of 1460–1250 cm<sup>-1</sup> that are assigned to ring modes of the aromatic rings [12,24]. The bands at 1160 and 1098 cm<sup>-1</sup> are assigned to C–O stretching vibrations. Based on these FTIR results, it is expected that the interaction of RR-120 dye with the SP biosorbent should occur with the OH, NH<sub>2</sub>, C=O and COO groups and at the aromatic group present in the biomass, as previously reported in the literature [12,24,28,31]. In addition,

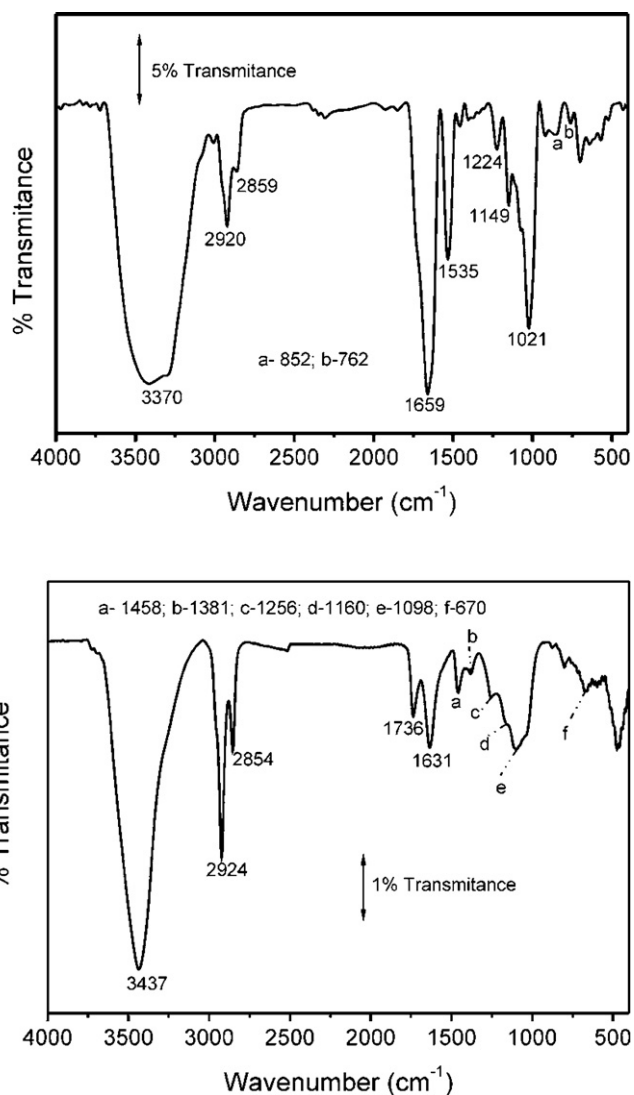


Fig. 1. FTIR spectra for: (A) SP; (B) AC.

FTIR spectra were obtained after the adsorption of RR-120 dye on the SP and AC adsorbents. However, the wavenumbers of the vibrational bands were practically the same as seen in the adsorbents without contact with the adsorbate, indicating that the interaction of the dye with the adsorbents presented low energy [24]. This result is consistent with the changes in adsorption enthalpy discussed in Section 3.5.

Supplementary Table 2 shows the proximal and centesimal (obtained from EDS analysis) compositions of *S. platensis* microalgae. As can be seen in Supplementary Table 2, *S. platensis* is composed of a variety of biomolecules, and the major elements on its surface are C, N, O, P and S. The point of zero charge (pH<sub>ZPC</sub>) of *S. platensis* microalgae is 7.0, as demonstrated in our recent study [31].

Based on the results of FTIR and EDS analysis, it can be stated that the *S. platensis* adsorbent contains functional groups, such as, carboxyl, hydroxyl, sulphate, phosphate, aldehyde and ketone [27–32]. On the other hand, the commercial activated carbon adsorbent presents OH, COOH and aromatic groups [11,12,23,24]. These chemical groups can mediate the interaction between the RR-120 textile dye and the adsorbent in aqueous solution.

The textural properties of the SP and AC adsorbents are presented in Supplementary Table 3. As expected, the superficial area and total pore volume of the AC adsorbent were much higher

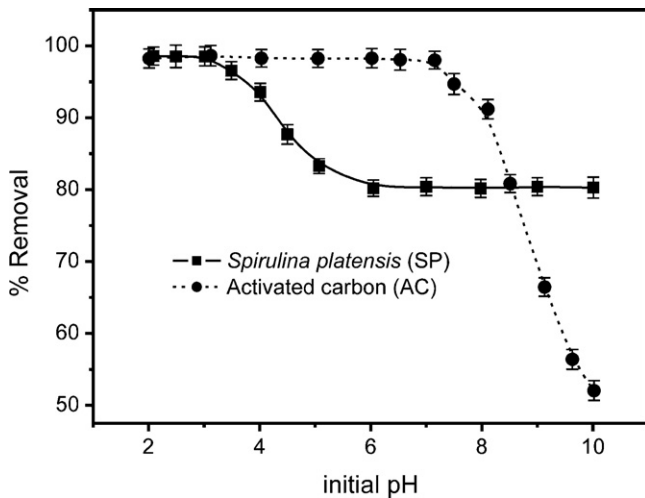


Fig. 2. Effect of pH on the adsorption of RR-120 dye on SP and AC adsorbents.

than those of the SP biomass [12]. The activated carbon adsorbent presents several micropore structures that are responsible for its higher superficial area and the greater volume of  $N_2$  adsorbed. On the other hand, biomass materials present lower superficial area and lower total pore volume when compared with activated carbons [3,4]. However, biomass adsorbents usually present a larger average pore diameter when compared with activated carbons [3,4,11,12]. This fact could facilitate the accommodation of more dye molecules in the pores of the biomass when compared with activated carbon, as previously reported in the literature [3,4,11,12].

### 3.2. Effects of acidity on adsorption

One of the most important factors that influences the adsorption of a dye on a solid adsorbent is pH [3,4]. Different dyes will present different ranges of suitable pH depending on which adsorbent is used. The effects of initial pH on the percentage of removal of RR-120 dye in solution ( $50 \text{ mg L}^{-1}$ ) using the SP and AC adsorbents were evaluated within the pH range between 2 and 10 (Fig. 2).

For the SP adsorbent, in the range of pH from 2.0 to 3.0, the percentage of dye removal was practically unchanged. In the range from pH 7.0 to 10.0, the decrease in the percentage of dye removal was only 0.1%, and the percentage of dye removal was also decreased by 18.2% in the range of pH 2.0–10.0. This may have occurred because, under acidic conditions (pH 2.0–3.0), the OH,  $\text{NH}_2$ , C=O and COO groups are protonated [3,4,24]. As consequence, the SP surface was positively charged ( $\text{pH}_{\text{pzc}} 7.0$ ). Coupled to this, the RR-120 sulphonate groups ( $\text{D-SO}_3\text{Na}$ ) were converted to anionic dye ions ( $\text{D-SO}_3^-$ ). It should be stated that the RR-120 dye did not present any colour changes in the pH range of 2.0–10.0, since it is a dye that belongs to the reactive dye class. Moreover, RR-120 dye possesses six sulphonate groups that make it readily soluble in water, even in extremely acidic medium, since its  $\text{pK}_3$  is lower than zero [24]. In this manner, electrostatic attraction occurs between the dye's sulphonate groups and the functional groups on the surface of *S. platensis*.

For the AC adsorbent, the percentage of dye removal decreased by less than 0.1% in the pH interval from 2.0 to 7.0. From pH 7.0 to 10.0, the decrease in the percentage of RR-120 dye removal was 44.3%. These results indicate that the activated carbon could be used within the pH range of 2.0–7.0 without presenting a remarkable difference on the percentage of dye removal, as previously observed in the literature [12,23,24]. On the other hand, the maximum removal of RR-120 dye took place in the pH interval of 2.0–3.0. The decrease

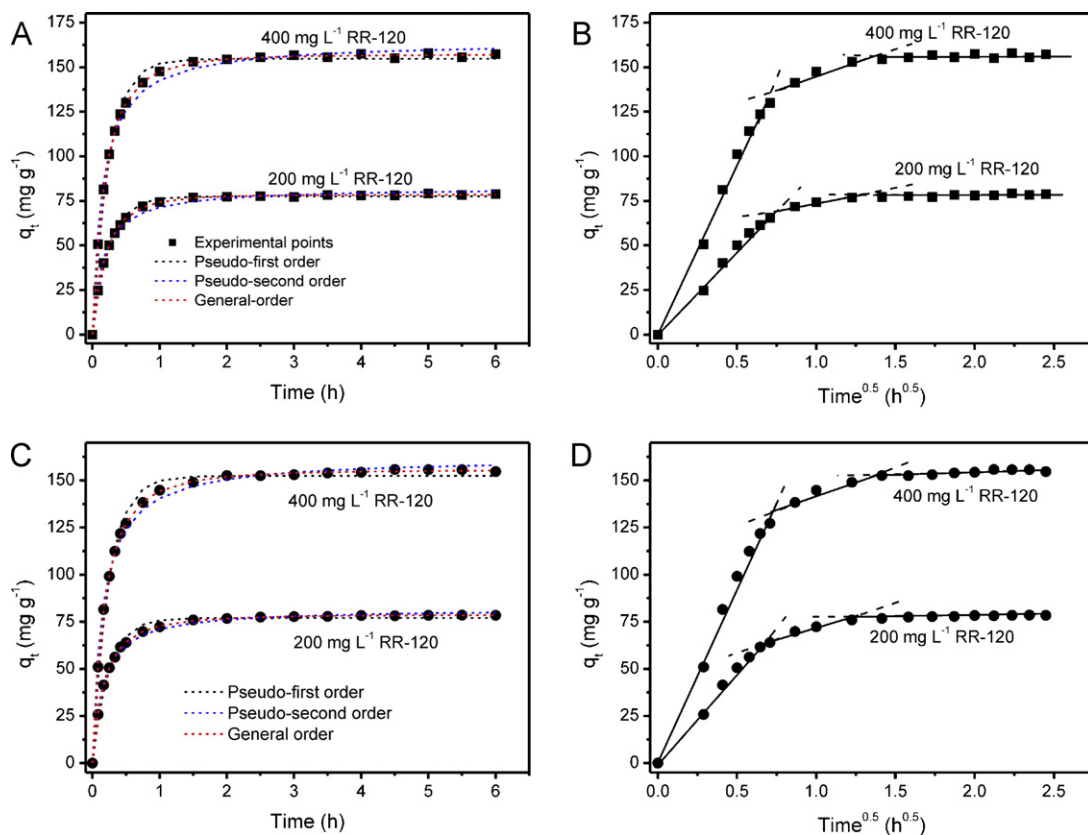


Fig. 3. Kinetic adsorption curves for RR-120 uptake at 298 K on SP and AC adsorbents. (A and B) SP; (C and D) AC.

in the percentage of dye removal with an increase in the pH of the dye solution was also previously observed using the alga *Stoechospermum marginatum* with acid orange II dye [19], the adsorption of Reactive Red 120 by the alga *Chara contraria* [51], the removal of Remazol Brilliant Blue R from aqueous solution using the green algae *Scenedesmus quadricauda* immobilised in alginate gel beads [52] and the removal of Lanaset Red G dye from aqueous solution using the alga *C. contraria* [53].

In order to continue this work, the initial pH of the RR-120 dye solution was fixed at pH 2.0 for the SP adsorbent and pH 6.0 for the AC adsorbent.

### 3.3. Kinetic studies

Adsorption kinetic studies are important in the treatment of dye-containing aqueous effluents because they provide valuable information on the mechanism of the adsorption process [50,54].

To evaluate the kinetics of adsorption of RR-120 dye using the SP and AC adsorbents, the non-linear pseudo-first order, pseudo-second order and general order kinetic adsorption models were tested, as shown in Fig. 3. The kinetic parameters for the three kinetic models are listed in Supplementary Table 4. Taking into account that the experimental data were fitted to non-linear kinetic models, an error function ( $F_{\text{error}}$ ) was used to evaluate the fitting of the experimental data. A lower  $F_{\text{error}}$  indicates a smaller difference in the  $q$  calculated by the model and the experimentally measured  $q$  [21–25,49] (see Supplementary Material, Eq. (20)). It should be pointed out that the  $F_{\text{error}}$  utilised in this work takes into account the number of fitted parameters (see Supplementary Material,  $p$  term of Eq. (20)), since it is reported in the literature [54,55] that the best fit of the results depends on the number of parameters contained in a non-linear equation. For this reason, the number of fitted parameters should be considered in the calculation of  $F_{\text{error}}$ . In addition, the  $F_{\text{error}}$  values are in agreement with the adjusted  $R^2$  values. However  $R^2$  values are limited to the range from 0 to 1, so verifying the difference in the experimentally measured  $q$  compared to the value of  $q$  given by the model is biased [55].

In order to compare the different kinetic models, the  $F_{\text{error}}$  of each individual model was divided by the  $F_{\text{error}}$  of the minimum value ( $F_{\text{error}}$  ratio). It was found that the minimum  $F_{\text{error}}$  values were obtained with the general order kinetic model. The pseudo-first order kinetic model presented  $F_{\text{error}}$  ratio values ranging from 3.52 to 4.71 (SP) and 6.34 to 7.33 (AC). Also, for the pseudo-second order model, the  $F_{\text{error}}$  ratio values ranged from 5.12 to 5.30 (SP) and 4.63 to 4.58 (AC). These results clearly indicate that the general order kinetic model better explains the adsorption process of RR-120 dye using the SP and AC adsorbents.

Taking into account that the general order kinetic equation presents different orders ( $n$ ) when the concentration of the adsorbate is changed (see Supplementary Table 4), it is difficult to compare the kinetic parameters of the model. Therefore, it is useful to use the initial sorption rate  $h_0$  [56] to evaluate the kinetics of a given model, using Eq. (3):

$$h_0 = k_n q_e^n \quad (3)$$

where  $h_0$  is the initial sorption rate ( $\text{mg g}^{-1} \text{h}^{-1}$ ),  $k_n$  is the rate constant ( $\text{h}^{-1}(\text{g mg}^{-1})^{n-1}$ ),  $q_e$  is the amount adsorbed at equilibrium ( $\text{mg g}^{-1}$ ) and  $n$  is the order of the kinetic model. It should be stressed that when  $n=2$ , this equation provides the same initial sorption rate first introduced by Ho and McKay [56]. It was observed that the initial sorption rate increased when increasing the initial dye concentration for all kinetic models, as expected, indicating that there is coherence within the experimental data. Taking into account that the kinetic data were better fitted to the general order kinetic model, since the order of an adsorption process should follow the same logic of a chemical reaction where the

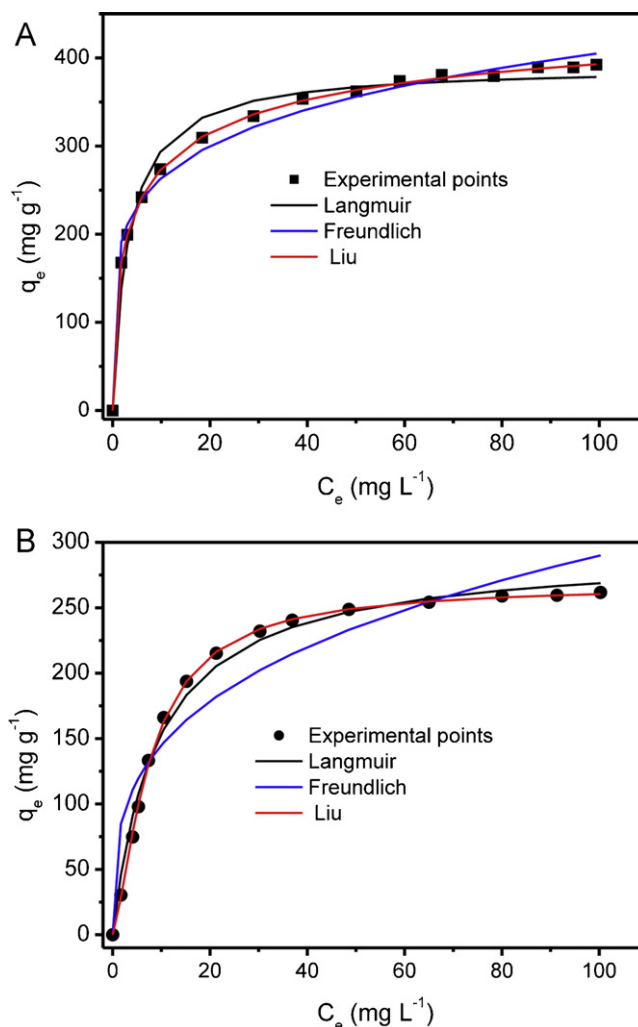


Fig. 4. Isotherms of adsorption of RR-120 dye at 298 K. (A) SP; (B) AC.

order is experimentally measured [57] instead of being previously stipulated by a given model, more confident initial sorption rates ( $h_0$ ) were obtained by the general order kinetic model.

The intra-particle diffusion model [41] was also used to verify the influence of mass transfer resistance on the binding of RR-120 dye to the SP and AC adsorbents (Supplementary Table 4 and Fig. 3B and D). The intra-particle diffusion constant,  $k_{\text{id}}$  ( $\text{mg g}^{-1} \text{h}^{-0.5}$ ), can be obtained from the slope of the plot of  $q_t$  versus the square root of time. These figures show the plots of  $q_t$  versus  $t^{1/2}$ , with three linear sections for the RR-120 dye using the SP and AC adsorbents. These results imply that the adsorption processes involve more than one sorption rate [50]. For both adsorbents, the adsorption process exhibited three stages, which can be attributed to each linear section of the plots in Fig. 3B and D. The first linear section was attributed to the diffusional process of the dye to the adsorbent surface [50]; hence, it was the fastest sorption stage. The second section, ascribed to intra-particle diffusion, was a delayed process [50]. The third stage may be regarded as diffusion through smaller pores, which is followed by the establishment of equilibrium [50].

It was observed in Fig. 4 that the minimum contact time required for RR-120 dye to reach equilibrium with the SP and AC adsorbents was about 2 h for both adsorbents. In order to continue this work, the contact time between the SP and AC adsorbents with RR-120 dye was fixed at 3.0 h using both adsorbents. The increased contact time utilised in this work was used to guarantee

that RR-120 dye equilibrium would be attained even at higher adsorbate concentrations [11,12].

### 3.4. Equilibrium studies

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed by the adsorbent ( $q_e$ ) and the adsorbate concentration remaining in the solution after the system attains equilibrium ( $C_e$ ), keeping the temperature of the process constant [15,16]. The adsorption parameters of equilibrium models often provide some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent by the adsorbate. In this study, the Langmuir [42], Freundlich [43] and Liu et al. [44] isotherm models were tested.

The adsorption isotherms were carried out from 298 to 323 K with RR-120 dye on the two adsorbents (SP and AC), and were performed using the best experimental conditions described above (see Supplementary Table 5, and Fig. 4). Fig. 4 shows the adsorption isotherms of RR-120 dye using SP and AC adsorbents at 298 K. Based on the  $F_{\text{error}}$  (see Supplementary Table 5), the Liu model was the best isotherm model for both adsorbents at all six temperatures studied. The Liu model showed (Supplementary Table 5) the lowest  $F_{\text{error}}$  values, which means that the  $q$  fit by the isotherm model was close to the  $q$  measured experimentally.

In order to compare the different equilibrium isotherm models, the  $F_{\text{error}}$  of each individual model was divided by the  $F_{\text{error}}$  of minimum value ( $F_{\text{error}}$  ratio). The Freundlich isotherm presented  $F_{\text{error}}$  ratio values ranging from 5.50 to 8.82 (SP) and from 13.17 to 23.80 (AC). The Langmuir isotherm model presented  $F_{\text{error}}$  ratio from 7.01 to 9.01 (SP) and from 4.77 to 12.73 (AC). These results of the  $F_{\text{error}}$  ratio analysis clearly indicate that the Liu isotherm model best explain the equilibrium of adsorption of RR-120 dye on the SP and AC adsorbents in the temperature range of 298 to 323 K.

The Langmuir isotherm model is based on the following principles [42]: adsorbates are chemically adsorbed at a fixed number of well-defined sites; each site can only hold one adsorbate species; all sites are energetically equivalent; there are no interactions between the adsorbate species. The Freundlich isotherm model assumes that the concentration of the adsorbate on the adsorbent surface increases with the adsorbate concentration. Theoretically, using this expression, an infinite amount of adsorption can occur [43]. The Liu isotherm model is a combination of the Langmuir and Freundlich isotherm models; therefore, the monolayer assumption of Langmuir model is ruled out and the infinite adsorption assumption that originates from the Freundlich model is also discarded. The Liu model [44] predicts that the active sites of the adsorbent cannot present the same energy. Therefore, the adsorbent may present active sites preferred by the adsorbate molecules for occupation [44]; however, saturation of the active sites should occur unlike in the Freundlich isotherm model. Taking into account that the adsorbents presented in this study have different functional groups (see Section 3.1), it is expected that the activate sites of the adsorbent will not have the same energy.

The maximum amount of the RR-120 dye adsorbed ( $Q_{\text{max}} = 482.2 \text{ mg g}^{-1}$ ) by the SP adsorbent was higher than the maximum amount by the adsorbed commercial activated carbon ( $Q_{\text{max}} = 267.2 \text{ mg g}^{-1}$ ). This may be attributed to a higher number of activated sites available in the microalgae when compared with the activated carbon. In the FTIR results (see Fig. 1), it can be noted that the amount of organic functional groups in SP (Fig. 1A) is greater than the residual organic groups present in the AC adsorbent (Fig. 1B). In addition, it was possible to verify that SP possessed protein (65.7%), lipids (7%) and carbohydrates (11.3%); see Supplementary Table 2.

When compared with other adsorbents presented in the literature [3,4,11,13,15,16,20,21,26,32] (see detailed a comparison

in Supplementary Table 6), SP presented satisfactory adsorption capacity, and can be alternatively considered for the removal of reactive dyes from aqueous effluents.

### 3.5. Thermodynamics of adsorption

As reported in the literature [11,12,24,25,29,31], the thermodynamic parameters related to the adsorption process, i.e. changes in Gibb's free energy ( $\Delta G$ ,  $\text{kJ mol}^{-1}$ ), enthalpy ( $\Delta H^\circ$ ,  $\text{kJ mol}^{-1}$ ) and entropy ( $\Delta S^\circ$ ,  $\text{J mol}^{-1} \text{ K}^{-1}$ ) can be estimated by the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\Delta G^\circ = -RT \ln(K) \quad (5)$$

The combination of Eqs. (4) and (5), gives:

$$\ln(K) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \quad (6)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is the absolute temperature (Kelvin) and  $K$  represents the equilibrium adsorption constants of the fitted isotherm. It has been reported in the literature that different adsorption equilibrium constants ( $K$ ) are obtained with different isotherm models [11,12,23,24,26,39,50,58–61]. The thermodynamic parameters of adsorption can be estimated from  $K_g$  (the Liu equilibrium constant), as previously reported in the literature [11,26]. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated from the slope and intercept of the linear plot of  $\ln(K)$  versus  $1/T$ .

The thermodynamic results are shown in Supplementary Table 7. The  $R^2$  values of the linear fit were at least 0.99, indicating that the values of enthalpy and entropy calculated for both adsorbents were confident. In addition, the magnitude of enthalpy was consistent with physical sorption for both adsorbents [62]. The type of interaction can be classified, to a certain extent, by the magnitude of the change in enthalpy. Physical sorption such as hydrogen bonding usually proves values  $<30 \text{ kJ mol}^{-1}$  [62]. Other physical sorption mechanisms such as van der Waals forces are usually  $4\text{--}10 \text{ kJ mol}^{-1}$ , hydrophobic bond forces about  $5 \text{ kJ mol}^{-1}$ , coordination exchange about  $40 \text{ kJ mol}^{-1}$  and dipole bond forces  $2\text{--}29 \text{ kJ mol}^{-1}$  [63]. On the other hand, chemical bond forces are usually  $>80 \text{ kJ mol}^{-1}$  [63]. The values of adsorption ( $\Delta H^\circ$ ) obtained in this study ( $<20 \text{ kJ mol}^{-1}$ ) are consistent with hydrogen bond and dipole bond forces for both adsorbents.

Enthalpy changes ( $\Delta H^\circ$ ) indicate that adsorption followed an exothermic process. Negative values of  $\Delta G$  indicate that RR-120 dye adsorption by the SP and AC adsorbents was a spontaneous and favourable process at all the studied temperatures. The positive values of  $\Delta S^\circ$  confirmed a high preference of RR-120 molecules for the surface of the SP and AC adsorbents, and also suggested the possibility of some structural changes or readjustments in the dye-carbon adsorption complex occurring during the adsorption process [64].

### 3.6. Treatment of a simulated dye-house effluent

In order to verify the efficiency of SP and AC as adsorbents for the removal of dyes from textile effluents, two simulated dye-house effluents were prepared (see Supplementary Table 1) with different contents of dyes. The UV-vis spectra of the untreated effluents and effluents treated with SP and AC were recorded from 350 to 800 nm (Fig. 5). The area under the absorption bands from 350 to 800 nm were utilised to monitor the percentage of the dye mixture removed from the simulated dye effluents. The SP adsorbent removed 94.4 and 99.0% (Fig. 5) and the AC adsorbent removed 93.6 and 97.7% (Fig. 5) of the dye mixture in effluents A and B,

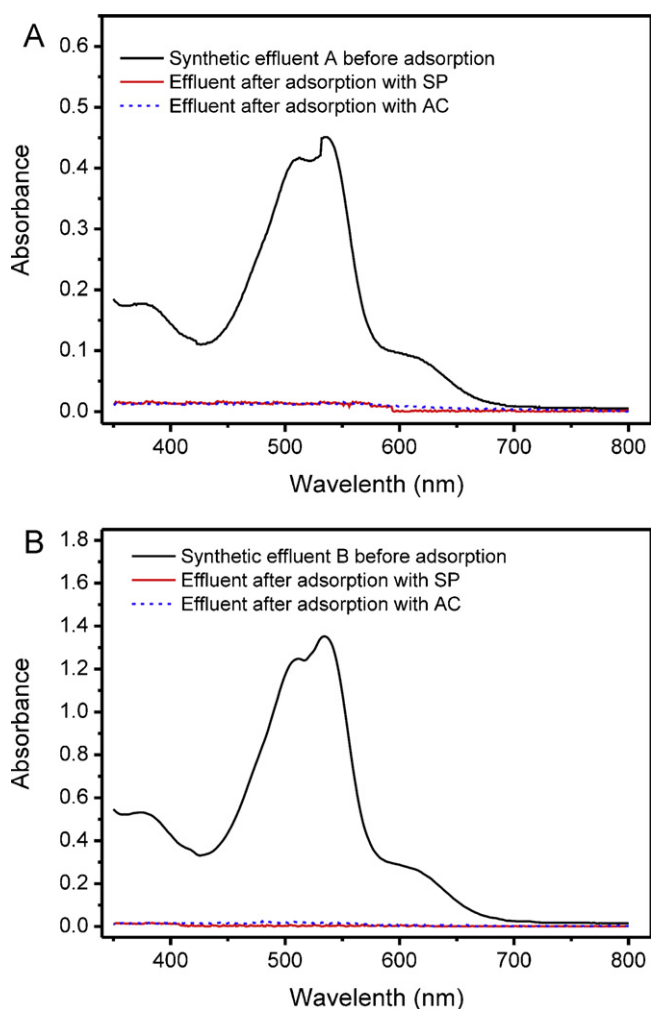


Fig. 5. UV-vis spectra of simulated dye effluents before and after adsorption treatment with SP and AC. For composition of effluents, see Supplementary Table 1.

respectively. The efficiency of the SP adsorbent for treating a simulated dye-house effluent presented slightly better performance when compared with the AC adsorbent. This result is in agreement with the previous results obtained in this study (please see Section 3.4). However, although the AC adsorbent presented slightly lower performance for treating a simulated dye-house effluent, it can be used as well as SP for real textile wastewater treatment (see Fig. 5). Based on these simulated effluent data, it is possible to infer that both the SP and AC adsorbents present good efficiency for the treatment of real wastewater effluents.

### 3.7. Desorption experiments

In order to evaluate the reuse of the SP and AC adsorbents, desorption experiments were carried out. Several eluents such as NaCl solutions ( $0.05\text{--}0.50\text{ mol L}^{-1}$ ), NaOH solutions ( $0.05\text{--}0.50\text{ mol L}^{-1}$ ) and a mixture of NaCl ( $0.05\text{--}0.50\text{ mol L}^{-1}$ ) +  $0.50\text{ mol L}^{-1}$  NaOH were tested for the regeneration of the loaded adsorbent (see Supplementary Table 8). For SP, it should be mentioned that  $0.30\text{--}0.50\text{ mol L}^{-1}$  NaOH immediately desorbed the dye taken up by the adsorbent. On the other hand, the recoveries of the adsorbent by aqueous NaCl at different concentrations as the regenerating solution did not occur efficiently even after 1 h of agitation (recoveries < 3%). The mixture containing NaCl ( $0.05\text{--}0.50\text{ mol L}^{-1}$ ) +  $0.10\text{ mol L}^{-1}$  NaOH presented fairly good desorption of the dye from SP (recoveries

$70.15\text{--}74.36\%$ ). The best elution efficiency was obtained with  $0.50\text{ mol L}^{-1}$  NaOH. This result confirms the thermodynamic parameters presented in Section 3.5 and the pH studies described above. RR-120 dye at pH 2.0 is electrostatically attracted to SP. This interaction was inhibited by the NaOH solution. For the AC adsorbent, the elution efficiency was lower than 13% for all the eluents tested, indicating that activated carbons could not be reutilised for adsorption purposes. On the other hand, SP eluted with  $0.50\text{ mol L}^{-1}$  NaOH was reutilised for the adsorption of RR-120 dye, attaining a sorption efficiency of about 93% in the second cycle, 90% in the third cycle and 88% in the fourth cycle of adsorption/desorption when compared with the first cycle of adsorption/desorption. Therefore, the use of SP for dye adsorption could be economically viable since regeneration of the adsorbent is feasible.

## 4. Conclusions

*S. platensis* and activated carbon were good adsorbents for the removal of Reactive Red 120 (RR-120) textile dye from aqueous solutions. The adsorbent materials were characterised by FTIR spectroscopy, SEM and  $\text{N}_2$  adsorption/desorption curves.

The most appropriate conditions were established with respect to pH and contact time to saturate the available sites located on the adsorbent surface. Four kinetic models were used to adjust the adsorption, and the best fit was the general order kinetic model. The equilibrium isotherm of the RR-120 dye was obtained, and these data fit best to the Liu isotherm model. The maximum adsorption capacities were  $482.2$  and  $267.2\text{ mg g}^{-1}$  for SP and AC, respectively. The thermodynamic parameters of adsorption ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G$ ) were calculated. The magnitude of the enthalpy of adsorption was compatible with a physical interaction of the RR-120 dye with both the SP and AC adsorbents. For the treatment of simulated industrial textile effluents, the SP and AC adsorbents presented good performance, removing 97.1 and 96.5%, respectively, of a dye mixture in media containing high saline concentrations.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.09.026>.

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