

KINETICS STUDIES OF ADSORPTION OF RR-120 DYE USING *Spirulina platensis* MICROALGAE AND COMMERCIAL ACTIVATED CARBON AS ADSORBENTS FROM AQUEOUS EFFLUENTS

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ABSTRACT: Comparative study of the removal of the dye Reactive Red 120 (RR-120) from aqueous effluents from textile industry using microalgae *Spirulina platensis* (SP) and commercial active carbon (AC) were carried out. The batch adsorption systems were evaluated with respect to pH, agitation time, temperature and initial concentration of the dye. The maximum adsorption capacity for dye RR-120 were found at pH 2 and 298K. The general kinetic model was the most appropriate to explain the adsorption of RR-120 using SP and CA. The SP and AC adsorbents showed good performance for treatment of simulated textile industrial effluents by removing from 94.4 to 99.0% and from 93.6 to 97.7%, respectively, of dye mixtures in high saline concentrations.

KEYWORDS: Reactive Red 120; adsorbent; effluent.

1. INTRODUCTION

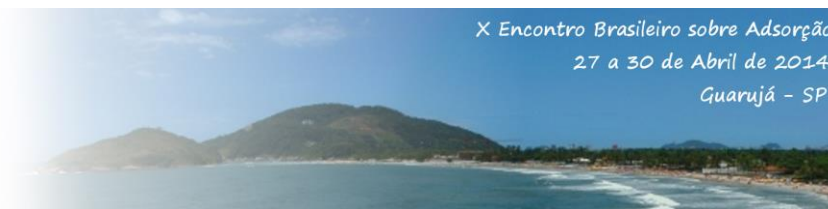
Dyes are used by different industries to colour their final products. The production of these products leads to the formation of dye-contaminated wastewater. The textile industry is responsible for the use of 30% of synthetic dyes (Hessel *et al.*, 2007).

The dye-containing wastewater discharged from these industries can adversely affect the aquatic environment by impeding light penetration and inhibiting the photosynthesis of aqueous flora (Cardoso *et al.*, 2011a; Cardoso *et al.*, 2011b). Moreover, the effects of these dyes can result in allergy, dermatitis, skin irritation (Brookstein, 2009) and also induce cancer (Carneiro *et al.*, 2010) and mutation in humans (Carneiro *et al.*, 2010; Lima *et al.*, 2007).

The effluents from the textile industry must be carefully treated before being discharged into

environment (Machado *et al.*, 2011, Cardoso *et al.*, 2011c). This has led to an increase in demand for eco-friendly technologies to remove dyes from aqueous effluents (Srinivasan *et al.*, 2010; Machado *et al.*, 2011; Cardoso *et al.*, 2011c).

Adsorption is one of the most commonly employed techniques for the removal of synthetic dyes from aqueous effluents (Somasekhara, *et al.*, 2012; Vargas *et al.*, 2012) due its simplicity and high efficiency, as well as the availability of a wide range of adsorbents that can be utilised (Machado *et al.*, 2011a; Somasekhara *et al.*, 2012; Vargas *et al.*, 2012; Royer *et al.*, 2009; Silva *et al.*, 2011). Adsorption transfers dye molecules from the aqueous effluent to the solid phase, remarkably decreasing dye bioavailability to living organisms (Machado *et al.*, 2011a; Cardoso *et al.*, 2011c). After treatment, the decontaminated effluent can be released to the environment or the water can be



re-used in the industrial processes (Royer *et al.*, 2009).

The blue-green algae *Spirulina platensis* is available in large quantities because it is cultivated worldwide; its annual production is about 2000 tons (Elekli and Yavuzatmaca, 2009; Elekli *et al.*, 2010). The biomass contains a variety of functional groups such as carboxyl, hydroxyl, sulphate, phosphate and other charged groups that can mediate pollutant binding (Seker *et al.*, 2009; Dotto *et al.* 2012).

This microalgae has been successfully employed to remove heavy metals (Elekli *et al.*, 2010; Elekli and Bozkurt, 2011) and food dyes (Dotto *et al.*, 2012a, Dotto *et al.*, 2012b) 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 (Calvete *et al.*, 2010) 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.

2. MATERIAL AND METHODS

2.1 Solutions and reagents

All solutions were prepared using deionised water. Reactive Red 120 dye (RR-120) was obtained from Sigma–Aldrich (Switzerland) as a commercially available textile dye, with 80% dye content, and was used without further treatment.

The stock solution (5.00 g L⁻¹) of RR-120 was prepared by dissolving the dye in deionised water. The working solutions were obtained by diluting the stock solution to the required concentrations. A 0.50 mol L⁻¹ NaOH or a 0.50 mol L⁻¹ HCl was used to adjust the pH of the solutions. The pH of the solutions was measured using a Schott Lab 850 set pH meter (Germany).

2.2 Adsorbents preparation and characterisation

S. platensis microalgae and commercial activated carbon were used as adsorbents in this work. The commercial activated carbon (Merck,

Germany) with a particle size of <90 µm was used in comparison with *S. platensis*.

S. platensis (strain LEB-52) was cultivated in a 450 L open outdoor photo-bioreactor, under uncontrolled conditions in the southern region of Brazil. During these cultivations, water was supplemented with 20% Zarrouk synthetic medium (Costa *et al.*, 2004). 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 airflow.

The drying conditions were: air temperature 60 °C, air velocity 1.5 m s⁻¹, relative humidity between 7% and 10% and load in the tray of 4 kg m⁻² (Oliveira *et al.*, 2009). The dried biomass was ground by a mill (Wiley Mill Standard, No. 03, USA) and sieved to obtain discrete particle size ranging from 68 to 75 µm. *S. platensis* was characterised according to the centesimal chemical composition and energy dispersive X-ray spectroscopy (EDS) (Pioneer).

The SP and AC were characterised using Fourier transform infrared spectrophotometer (FTIR) (Varian spectrometer, model 640-IR). The spectra were obtained with a resolution of 4 cm⁻¹ with 100 cumulative scans.

The surface analyses and porosity were carried out using 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 Pa. For area and pore calculations, the multi-point BET and BJH (Vaghetti *et al.*, 2003) methods were used.

2.3 Adsorption studies

For batch adsorption experiments, 50.0 mg of adsorbents were placed in 50 mL tubes containing 20.0 mL of the dye solutions (50.00–1200.0 mg L⁻¹), which were agitated for a suitable time (0.0833–6.00 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, the contents of the flasks were transferred to centrifuge tubes and then centrifuged at 10,000 rpm for 10 min. Aliquots, between 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 measured using UV/visible spectrophotometer at 534 nm. The adsorption capacity and the percentage dye removal were evaluated using Equation (1) and (2), respectively.

$$q_e = \frac{(C_o - C_f)}{X} \quad (1)$$

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

Where q is the amount of dye adsorbed by the adsorbent (mg g^{-1}), C_o is the initial dye concentration (mg L^{-1}), C_f is the dye concentration (mg L^{-1}) after the batch adsorption study and X is the adsorbent dosage (g L^{-1}).

2.4 Kinetic adsorption models

In a chemical reaction, the rate law's exponents are generally unrelated to the coefficients of chemical equations, but are sometimes the same by coincidence (Liu and Shen, 2008; Liu and Liu, 2008). The pseudo-first order (Equation 3), pseudo-second order (Equation 4), general order equation (Equation 5) and intra-particle diffusion (Equation 6) models were used to evaluate the kinetics RR-120 on SP and CA.

$$q_t = q_e [1 - \exp(-k_1 \cdot t)] \quad (3)$$

$$q_t = \frac{q_e^2 k_2 t}{[k_2 (q_e) \cdot t + 1]} \quad (4)$$

$$q_t = q_e - \frac{q_e}{[k_N (q_e)^{n-1} \cdot t \cdot (n-1) + 1]^{1/n}} \quad (5)$$

$$q_t = k_{id} \sqrt{t} + C \quad (6)$$

In these equations, q_t is the amount of adsorbate adsorbed by adsorbent at a particular time, t , in mg g^{-1} ; q_e is the amount of adsorbate adsorbed by adsorbent at equilibrium in mg g^{-1} ; k_N represents the rate constant, k_1 and k_2 are the pseudo-first order and pseudo-second order rate

constants, respectively; n is the order of adsorption in relation to the effective concentration of the adsorption active sites at the surface of adsorbent; k_{id} is intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{h}^{-0.5}$); C is a constant related to the thickness of boundary layer (mg g^{-1}).

2.5 Simulated dye-house effluent

Two synthetic dye-house effluents (effluents A and B) 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 mostly used in the textile industry. According to the technical information obtained from a dye-house, typically 10–50% (Hessel *et al.*, 2007) 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 (Machado *et al.*, 2011,50]. The concentrations of the dyes in effluent A are 20.0, 5.0, 5.0, 5.0 and 5.0 mg L^{-1} for Reactive Red 120, Reactive Orange 16, Reactive Black 5, Cibacron Brilliant Yellow 3G-P and Direct Blue 53, respectively. The respective concentration for effluent B are 60.0, 15.0, 15.0, 15.0 and 15.0 mg L^{-1} . The auxiliary chemicals selected to imitate an exhausted dye bath with their concentration for the two effluents are: Na_2SO_4 (100.0 mg L^{-1}), NaCl (100.0 mg L^{-1}), Na_2CO_3 (150.0 mg L^{-1}), CH_3COONa (150.0 mg L^{-1}) and CH_3COOH (600.0 mg L^{-1}). The effluents are adjusted to pH of 2.0.

3. RESULTS AND DISCUSSION

3.1 Characterization of *S. platensis* and commercial activated carbon

The FTIR spectrum of *S. platensis* shows OH bond stretching mixed with the NH_2 group at 3370 cm^{-1} (intense and broad band (Cardoso *et al.*, 2011c; Calvete *et al.*, 2009). The bands at 2920 and 2859 cm^{-1} are related to asymmetric and symmetric stretching of CH_2 groups, respectively (Cardoso *et al.*, 2011c; Calvete *et al.*, 2009). Scissor bending of the NH_2 group can be observed at 1659 and 1535 cm^{-1} (sharp and intense bands) (Elekli and Yavuzatmaca, 2009; Elekli and Bozkurt, 2011).

The bands at 1224 , 1149 , 1021 cm^{-1} can be assigned to the C-N stretch of amide or amine groups (Elekli *et al.*, 2010; Dotto *et al.*, 2012a).

The adsorption bands in the region 750–900 cm^{-1} can be linked with P-O, S-O and aromatic C-H stretching vibrations (Elekli *et al.*, 2010). Shows the FTIR vibrational spectra of the commercial activated carbon. The intense absorption band at 3437 cm^{-1} is assigned to O-H bond stretching (Cardoso *et al.*, 2011c, Calvete *et al.*, 2009). The two CH_2 stretching bands at 2924 and 2854 cm^{-1} are assigned to asymmetric and symmetric stretching of CH_2 groups (Cardoso *et al.*, 2011c; Calvete *et al.*, 2009).

The sharp band at 1736 cm^{-1} is assigned to the carbonyl group of carboxylic acid (Cardoso *et al.*, 2011c). The sharp intense peak at 1631 cm^{-1} is assigned to aromatic C-C ring stretching (Cardoso *et al.*, 2011c; Calvete, 2009).

Furthermore, there are several small bands and shoulders in the range of 1460–1250 cm^{-1} that are assigned to ring modes of the aromatic rings (Cardoso *et al.*, 2011c; Calvete *et al.*, 2009). The bands at 1160 and 1098 cm^{-1} are assigned to C-O stretching vibrations.

It is expected, therefore, that the interaction of RR-120 dye with the SP biosorbent should occur with the OH, NH_2 , C=O and COO^- groups and at the aromatic group present in the biomass, as (Cardoso *et al.*, 2011c; Calvete *et al.*, 2009; Elekli *et al.*, 2010; Dotto *et al.*, 2012a).

FTIR spectra were also obtained after the adsorption of RR-120 dye on the SP and AC adsorbents. However, the wavenumbers of the vibrational bands were similar as seen in the adsorbents without contact with the adsorbate, indicating that the interaction of the dye with the adsorbents is of low energy (Calvete *et al.*, 2009).

S. platensis has many biomolecules; C, N, O, P and S are the major elements on its surface. The point of zero charge (pHzpc) of *S. platensis* microalgae is 7.0 as shown in our recent study (Dotto *et al.*, 2012a).

Based on the results of FTIR, it can be stressed that *S. platensis* contains functional groups such as carboxyl, hydroxyl, sulphate, phosphate, aldehyde and ketone (Elekli and Yavuzatmaca, 2009; Dotto *et al.*, 2012b).

Contrarily, the commercial activated carbon adsorbent has OH, COOH and aromatic groups (Machado *et al.*, 2011; Cardoso *et al.*, 2011c; Calvete *et al.*, 2010; Calvete *et al.*, 2009). These chemical groups can mediate the interaction between the RR-120 textile dye and the adsorbent in aqueous solution.

The superficial area and total pore volume of the AC were higher than those of the SP biomass (Cardoso *et al.*, 2011c). The activated carbon adsorbent possesses several micropore structures that are responsible for its higher superficial area and the greater volume of N_2 adsorbed.

One of the intriguing factors that influences the adsorption of a dye on a solid adsorbent is pH (Cardoso *et al.*, 2011a). Different dyes have different ranges of suitable pH depending on the adsorbent being used. The effects of initial pH on the percentage of removal of RR-120 dye in solution (50 mg L^{-1}) using the SP and AC adsorbents were evaluated within the pH range of 2 and 10.

For the SP adsorbent, in the pH range of 2.0 to 3.0, the percentage of dye removal was practically unchanged. In the pH range of 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 pH range of 2.0–10.0.

This may have occurred because under acidic conditions (pH 2.0–3.0), the OH, NH_2 , C-O and COO^- groups are protonated (Cardoso *et al.*, 2011a; Cardoso *et al.*, 2011b; Calvete *et al.*, 2009). As a result, the SP surface was positively charged (pHpzc

In addition to this, the RR-120 sulphonate groups ($\text{D-SO}_3\text{Na}$) were converted to anionic dye ions (D-SO_3^-). It should be mentioned that the RR-120 dye did not show any colour changes in the pH range of 2.0–10.0, since it belongs to the reactive dye class. Moreover, RR-120 dye has six sulphonate groups that make it readily soluble in water, even in acidic medium, since its pKa is < 0 (Calvete *et al.*, 2009). 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 $< 0.1\%$ 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%. This indicates that the activated carbon could be used within the pH range of 2.0–7.0 without a remarkable difference on the percentage of dye removal, as previously reported (Cardoso *et al.*, 2011c; Calvete *et al.*, 2010; Calvete *et al.*, 2009).

The decrease in the percentage of dye removal with an increase in the pH of the dye solution was also reported using the alga

Stoechospermum marginatum with acid orange II dye (Doğar *et al.*, 2010). The adsorption of RR-120 by the alga *Chara contraria* (Elekli *et al.*, 2012) the removal of Remazol Brilliant Blue R from aqueous solution using the green algae *Scenedesmus quadricauda* immobilised in alginate gel beads (Ergene *et al.*, 2009) and the removal of Lanaset Red G dye from aqueous solution using the alga *C. contraria* (Elekli and Bozkurt, 2011) were also reported.

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.

Taking into account that the general order kinetic equation has different orders (n) when the concentration of the adsorbate is changed, it is difficult to compare the kinetic parameters of the model. Therefore, it is useful to use the initial sorption rate h_0 (Ho and McKay, 1988) to evaluate the kinetics of a given model, using Equation (7):

$$h_0 = K_N \cdot q_e^n \quad (7)$$

where h_0 is the initial sorption rate ($\text{mg g}^{-1} \text{h}^{-1}$), K_N is the rate constant ($\text{h}^{-1}(\text{g mg}^{-1})^n$), q_e is the amount adsorbed at equilibrium (mg g^{-1}) and n is the order of the kinetic model. It should be pointed out that when $n = 2$, this equation provides the same initial sorption rate first introduced by Ho and McKay (1988). It was noticed 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 order is experimentally measured by Chang (2011) 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 (Weber-Jr. and Morris, 1963) was also used to verify the influence of mass transfer resistance on the binding of RR-120 dye to the SP and AC. The intra-particle diffusion constant, k_{id} ($\text{mg g}^{-1} \text{h}^{-0.5}$) was obtained from the slope of the plot of q_t versus the square root of time. This means that the adsorption processes involved more than one sorption rates (Alencar *et al.*, 2012). The adsorption exhibited

three stages. The first stage was attributed to the diffusional process of the dye to the adsorbent surface (Alencar *et al.*, 2012), which was the fastest sorption stage. The second stage, ascribed to intra-particle diffusion, a delayed process (Alencar *et al.*, 2012). The third stage may be regarded as diffusion through smaller pores, which is followed by the establishment of equilibrium (Alencar *et al.*, 2012).

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 (Machado *et al.*, 2011a; CARDOSO *et al.*, 2011c).

3.2 Treatment of a simulated dye-house effluent

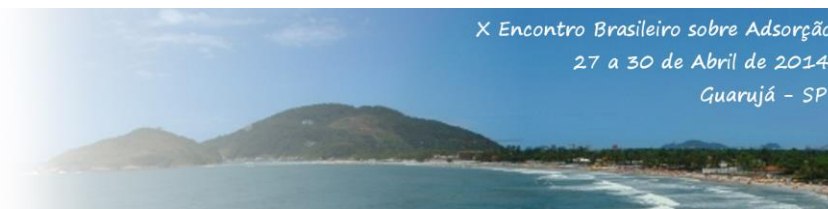
To investigate the capacity of SP and AC as adsorbents for the removal of dyes from textile effluents, two simulated dye-house effluents were used with different dye compositions. The UV/Vis spectra of the untreated effluents and effluents treated with SP and AC were recorded from 350 to 800 nm. The area under the absorption bands from 350 to 800 nm were used to monitor the percentage of the dye mixture removed from the simulated dye effluents. The SP adsorbent removed 94.4 and 99.0% and the AC adsorbent removed 93.6 and 97.7% of the dye mixture in effluents A and B, 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.

Although AC showed lower performance than SP for treating simulated dye-house effluents, however, it can be used for treatment of real textile wastewater. Based on the simulated effluent data, it is possible to infer that both the SP and AC have good efficiency for the treatment of real wastewater effluents.

4. CONCLUSIONS

S. platensis and activated carbon served as good adsorbents for the removal of RR-120 from aqueous solutions. The adsorbents were characterised using FTIR spectroscopy, SEM and N_2 adsorption/desorption curves. The suitable conditions were established in term of pH and contact time for the saturation of the available sites



on the adsorbent surface. Four kinetic models were used to explain the adsorption process, and the best fit was the general order kinetic model. The maximum adsorption capacities were 482.2 and 267.2 mg g⁻¹ for SP and AC, respectively. For the treatment of simulated industrial textile effluents, the SP and AC adsorbents showed good performance, removing 97.1 and 96.5%, respectively, of dye mixtures in high saline media.

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