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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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HIGHLIGHTS

- *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^{-1} 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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ABSTRACT

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^{-1} 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.

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 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 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 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 μm was used for comparison with *S. platensis*.

S. platensis (strain LEB-52) was cultivated in a 450 L 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 °C, air velocity 1.5 m s^{-1}, relative humidity between 7% and 10% and load in the tray of 4 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 μm. *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 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} 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 (50.00–1200.0 mg L^{-1}), which were agitated for a suitable period of 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, 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 (mg g^{-1}), C_0 is the initial dye concentration (mg L^{-1}), C_f is the dye concentration (mg L^{-1}) after the batch adsorption procedure and X is the adsorbent dosage (g L^{-1}).