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Research article

# The application of textile sludge adsorbents for the removal of Reactive Red 2 dye

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ABSTRACT

Sludge from the textile industry was used as a low-cost adsorbent to remove the dye Reactive Red 2 from an aqueous solution. Adsorbents were prepared through the thermal and chemical treatment of sludge originating from physical–chemical (PC) and biological (BIO) effluent treatment processes. The adsorbent characterization was carried out through physical–chemical analysis, X-ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, $pH_{PZC}$ determination, Boehm titration method, Brunauer–Emmett–Teller (BET) surface area analysis and scanning electron microscopy (SEM). Batch kinetic experiments and adsorption isotherm modeling were conducted under different pH and temperature conditions. The results for the kinetic studies indicate that the adsorption processes associated with these systems can be described by a pseudo-second-order model and for the equilibrium data the Langmuir model provided the best fit. The adsorption was strongly dependent on the pH but not on the temperature within the ranges studied. The maxima adsorption capacities were 159.3 mg $g^{-1}$ for the BIO adsorbent and 213.9 mg $g^{-1}$ for PC adsorbent at pH of 2 and 25 °C.



## 1. Introduction

The textile industry generates large volumes of liquid effluents containing dyes, mostly as residues of textile fiber dyeing processes. Such effluents must be properly treated, as they can cause serious environmental problems. The presence of dyes reduces the water transparency, which interferes with photosynthesis and therefore harms aquatic plant life (Fernández et al., 2010; Oliveira et al., 2007).

Dyes are recalcitrant molecules, being resistant to aerobic digestion, light, heat, and oxidizing agents. Some studies also show that they may be carcinogenic or mutagenic, particularly in the case of azo dyes and their by-products (Gupta and Suhas, 2009; Carneiro et al., 2010; McKay, 1996).

Adsorption is a separation and purification process that is broadly used to remove polluting substances which do not easily biodegrade. It is a promising technique and has received greater attention that other removal methods in recent decades (Jain et al., 2003; Ho and McKay, 2003).

Commercial-grade activated carbon is the most commonly used adsorbent for the removal of effluent color, due to its efficiency. However, its broader use is restricted due to its high cost. Moreover, the reuse or dispose of powdered activated carbons are difficult due to the very fine powder that can remain suspended in treated water during a long time. Thus, several alternative adsorbents have been studied in order to reduce the cost of this type of treatment (Crini, 2006; Bhatnagar and Jain, 2005; Gupta et al., 2003). An alternative adsorbent is considered to be of low-cost when minimal processing is required, it is abundant in nature, or it is derived from an industrial by-product (Gupta and Suhas, 2009; Bailey et al., 1999). Such adsorbents may be made of peat (Ho and McKay, 1998), seaweed (Vijayaraghavan and Yun, 2008), chitosan (Chang and Juang, 2004; Prado et al., 2004), leaves (Bhattacharyya et al., 2009), sawdust (Vijayaraghavan et al., 2009), agricultural industry waste (Mittal et al., 2010), peat (Allen et al., 2004) or sludge (Netpradit et al., 2004; Vasques et al., 2009), among others.

Sludge can be defined as the residue generated from an effluent treatment process. In primary treatment, which is characterized by physical–chemical processes, the resulting residue contains a mixture of inorganic compounds. On the other hand, secondary treatment involving biological processes results in a residue containing a complex mixture of non-digested organic compounds and

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dead microorganisms (Aksu and Akin, 2010; Smith et al., 2009; Fonts et al., 2012). However, the final characteristics of such a residue may vary greatly depending on the sludge origin, treatments applied and even the coagulating agents used (Smith et al., 2009; Annadurai et al., 2003; Khursheed and Kazmi, 2011).

Converting sludge into adsorbents may be of interest due to the potential value of the residue, and is of great significance considering the increasing amounts of sludge generated and the presence of more rigorous legislation that regulates its disposal and use (Smith et al., 2009). The conversion can be made through sludge pyrolysis. This process is characterized by decomposing organic matter in the absence of oxygen at between 300 and 900 °C while generating gas, a carbonous residue, and oils. The resulting gas and oils can be used as fuels while the solid residue can be burned for energy or used to produce low-cost adsorbents (Vasques et al., 2009; Werther and Ogada, 1999; Inguanzo et al., 2001; Fonts et al., 2009).

The removal of dyes from aqueous solution using alternative adsorbents has been extensively studied by several authors (Gupta and Suhas, 2009; Crini, 2006; Srinivasan and Viraraghavan, 2010). The removal of Reactive Red 2 (RR2) dye using sludge from several origins has been studied by Netpradit et al. (2003, 2004); Vasques et al. (2009); Babu et al. (2011); Geethakarthi and Phanikumar (2011).

Taking into account the above presented statements, the aim of this study was to evaluate the thermal treatment (through pyrolysis) and chemical treatment (with 0.1 M $H_2SO_4$) of sludge samples generated during the physical–chemical or biological treatment of textile effluents, in order to obtain adsorbents for the removal of Reactive Red 2 dye from aqueous solution. The effects of solution pH and temperature were also investigated. The thermodynamic parameters Gibbs free energy ($\Delta G^\circ$), adsorption heat ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were determined.

## 2. Materials and methods

### 2.1. Adsorbent preparation

Sludge generated by a Brazilian textile company was used to prepare the adsorbents. Sludge produced during physical–chemical (PC) or biological (BIO) effluent treatment were subjected to thermal and chemical treatment in order to obtain the adsorbents.

The raw sludge samples were firstly sun-dried for three days and then dried in an oven (Tecnal, TE-393/1) at 80 °C for approximately 4 h. Fractions with diameters of between 0.152 and 0.450 mm were selected for the experiments. Procedures for the thermal and chemical treatments were based on the work of Vasques et al. (2009).

#### 2.1.1. Thermal treatment

For the thermal treatment, approximately 40 g of raw sludge was placed in a stainless steel reactor attached to a muffle furnace (EDG, 3P-S 3000). The sample was heated in a closed system (Supplementary Material 1) at 500 °C under low vacuum in the muffle furnace (1) for 70 min. The gases released were condensed (2) and collected in a flask (3).

#### 2.1.2. Chemical treatment

For the chemical treatment, 1g of pyrolyzed material was placed in a 250 mL Erlenmeyer flask with 50 mL of a 0.1 M solution of $H_2SO_4$. The system was stirred at 115 rpm in an orbital shaker (Tecnal, TE-424) at 25 °C for 3 h. The resulting product was filtered through filter paper and left in the oven at 105 °C until a constant weight was obtained.

### 2.2. Adsorbent characterization

The physical–chemical properties of the adsorbents obtained were determined through X-ray fluorescence (XRF) spectroscopy (Shimadzu, EDX-700). The point of zero charge was estimated through an adapted version of the batch equilibrium method described by Babic et al. (1999). The adsorbents were analyzed by FTIR spectroscopy (Perkin Elmer, Spectrum 100) in order to determine the functional groups present. A scanning electron microscope (**JEOL**, **JSM-6390LV**) was used to observe the surface morphology of the material andBET surface area analysis (Autosorb 1C – Quantachrome)was performed in order to determine the textural properties.

The acid properties of adsorbents surface were determined by the method ofBoehm (1994). First, 0.5 g of adsorbent were mixed with 100 mL of different bases (0.05 M NaHCO3, 0.05 M Na2CO3 or 0.05 M NaOH) in flasks of 250 mL. The Erlenmeyer flasks were sealed and kept under stirring during 24 h at25 °C. The samples were filtered and aliquots of 10 mL were titrated with HCl 0.1 M.

### 2.3. Adsorbate solutions

Dye solutions were prepared by diluting a stock solution with distilled water. The pH of each solution was adjusted to the desired value by adding diluted $H_2SO_4$ or NaOH, with the aid of a pHmeter (Quimis, Q–400M2). Details about the chemical structure of the dye Reactive Red 2 and its main physical and chemical properties are presented in the Supplementary Material 2.

A UV–vis spectrophotometer (Shimadzu, 1240) was used to determine the dissolved dye RR2 concentrations. Calibration curves were built in order to determine the final concentration in solution after the adsorption experiments, measured at the longest adsorption wavelength for this dye ($\lambda_{max} = 538$ nm).

### 2.4. Equilibrium studies

#### 2.4.1. Effect of initial pH

The influence of solution pH was studied using 5 g $L^{-1}$ of adsorbent in solution. For each initial pH condition, this amount of adsorbent was placed in a 250 mL Erlenmeyer flask with 50 mL of 500 mg $L^{-1}$ dye RR2 solution. The system was stirred at 115 rpm in an orbital shaker at 25 °C for 15 h. The resulting dye solutions were then collected and analyzed using a UV–vis spectrophotometer and a pHmeter. The percentage of dye removed from the solution was calculated as follows:

$$\%removal = \frac{(C_o - C)}{C_o} \cdot 100 \quad (1)$$

where $C_0$ and $C$ are the initial and final dye concentrations (mg $L^{-1}$), respectively. All adsorption experiments were performed in duplicate.

#### 2.4.2. Adsorption isotherms

In order to obtain the adsorption isotherms 50 mL of dye RR2 solutions in different concentrations (see Table 1) and 5 g $L^{-1}$ of adsorbent were placed in 250 mL Erlenmeyer flasks for equilibrium tests. Samples were placed under constant stirring at 115 rpm in an orbital shaker, under different pH (2 and 4) and temperature (25 and 45 °C) conditions for 15 h, in order to guarantee the adsorption equilibrium. The samples were then decanted and aliquots of the supernatant solution were collected to obtain the final dye concentration.

The quantity of adsorbed dye $q$ (mg $g^{-1}$) was calculated through the mass balance relation: