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Adsorption of cationic and anionic azo dyes on sepiolite clay: Equilibrium and kinetic studies in batch mode

Sílvia C.R. Santos*, Rui A.R. Boaventura

Laboratory of Separation and Reaction Engineering—Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

In the present work, sepiolite clay adsorptive properties were investigated for textile azo dyes in aqueous solution. The clay (78 wt.% sepiolite) was characterized in terms of physical, textural, chemical and mineralogical properties. Basic Red 46 and Direct Blue 85 azo dyes were selected as adsorbates. Adsorption equilibrium data were successfully fitted to Freundlich and Langmuir equations. For Basic Red, the maximum adsorption capacities, predicted by the Langmuir model, were 110 mg/g (at 25 °C) and 310 mg/g (at 35 °C). The value obtained at 25 °C, matched perfectly the cation exchange capacity of the clay. For Direct Blue, the adsorption capacity was 332 mg/g. Adsorption equilibrium was also evaluated for Direct Blue dye in a synthetic effluent, containing salt and auxiliary dyeing chemicals. In this mixture, the amount of dye adsorbed by sepiolite decreased, but very considerable values were still reached (106 mg/g). Adsorption kinetics was studied and modeled. Homogeneous solid diffusion coefficient and effective pore diffusivities were calculated for both dyes. Sepiolite clay showed to be an advantageous adsorbent in terms of price and versatility, being effective under a wide pH range, for both anionic and cationic dyes. Its use as adsorbent does not require further purification or chemical modifications, which is beneficial for the environment and for the economy of the treatment.

1. Introduction

Textile industries are one of the largest consumers of water and hence producers of liquid effluents. The dyeing and finishing processes generate volumes of wastewaters in the range 45–450 m^3 per ton of product [1], containing salts, acids, bases, additives and unfixed dyes. A suitable treatment of these complex wastewaters should lead to a strong decline on the organic load, and desirably to a complete elimination of the residual color. The entrance of dyes into water bodies harms their aesthetic condition, compromising many water uses and affects aquatic life [2]. In particular, azo dyes and their derivatives are mutagenic and carcinogenic [3,4], posing serious risks to aquatic life and human health.

Biological and coagulation/flocculation processes are usually the most economical options to treat high volumes of wastewaters. Aerobic biological treatment is however ineffective against many dyes [5,6], and decolorization by anaerobic via can yield dangerous aromatic amines [7]. Color removal by coagulation using traditional iron and aluminium salts is not consistently effective [8] and produces a huge volume of sludge. Many alternative treatments have been proposed to remove effectively the dyes from the wastewaters, such as chemical reduction, membrane separation, chemical oxidation, advanced oxidation processes (AOPs). In spite of the good decolorization results achieved and the specific advantages or disadvantages of each one, the cost of implementation or operation is not attractive for the industry. Adsorption has been viewed as an economic and effective option for the removal of contaminants from aqueous solution. Adsorption by activated carbon is especially useful as post treatment, after activated sludge or coagulation/flocculation [9,10]. Combining a conventional process with a tertiary level treatment, wastewater characteristics can be polished in the final adsorptive removal and a safe discharge can be achieved. However, the use of activated carbon (granular or powdered) entails considerable acquisition and regeneration costs. From an environmental point of view, it is also worth noting the high energy that is spent in the production of activated carbons. As a contribution to overcome these problems and to achieve color removal in a cost-effective manner, a wide range of natural and waste materials, raw and chemically modified, have been proposed as alternatives [6,11–16]. In spite of the considerable research on this topic, the state of knowledge still presents limitations, such as low adsorption capacities for anionic adsorbates, safety risks

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* Corresponding author. Fax: +351 225081674.
E-mail address: scrs@fe.up.pt (S.C.R. Santos).

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related to matrices not completely immobilized (heavy metal or organic matter possible leaching) [15], inadequate grain size or mechanical properties and the need of chemical modifications to give or improve the sorption capacity [17].

Sepiolite is a natural hydrated magnesium silicate. Its structure is composed by alternation of blocks and cavities (tunnels) that grow up in the fibre direction [18]. Rectangular channels contain some exchangeable Ca and Mg cations and two types of water: bound water (molecules coordinating Mg atoms at the broken bond surfaces of the channels) and zeolitic water (clusters filling the empty space in the channels and hydrogen-bonded to the bound water) [19]. As the silica sheets are discontinuous, silanol groups (SiOH) are present at the border of each block in the external surface of the silicate.

The ability of sepiolite to uptake cationic dyes has been demonstrated in some works [20–23], although these studies have been mostly focused on methylene blue and crystal violet dyes, which are not typically used in textile industry. The adsorption of monovalent cationic species is a result of the cation exchange capacity of sepiolite, but also of its neutral sites, where basic dyes can be adsorbed [22]. Further treatments such as saturation with sodium or calcium [24] showed to enhance a little more the adsorption capacity of sepiolite for methylene blue.

Regarding anionic dyes, natural sepiolite provided relatively low adsorbed amounts of an azo acid dye [25]. In its untreated form, sepiolite was not also able to remove reactive dyes, requiring a chemical modification with a quaternary amine (hexadecyltrimethylammonium bromide, HTAB) in order to create a positive surface charge and provide suitable adsorption [17]. Literature is relatively restricted concerning direct dyes removal by sepiolite. This kind of dyes are mainly applied in cellulosic fibres and are still commonly used in industry (instead of reactive dyes), due to their lower cost and easy application [6].

In the present work, a sepiolite clay material, usually commercialized as absorbent for industrial spillages and cat and pet litters, was studied as adsorbent for cationic and anionic textile azo dyes. The clay was characterized (in terms of physical, mineralogical and chemical properties). Adsorption kinetics and equilibrium were studied and modeled.

2. Materials and methods

2.1. Dyes

Two commercial textile dyes, kindly supplied by Dystar, were studied in this work: Basic Red 46 (BR) and Direct Blue 85 (DB). Fig. 1 illustrates the molecular structures of the dyes. BR is a cationic dye, usually used for dyeing acrylic fibres. DB is a direct anionic dye, suitable for cotton, viscose and modal dyeing, but also applicable for polyamide, wool and silk. Both dyes are from the azo chemical class. Aqueous solutions were simply prepared by dissolving the required mass of dye (dried at 105 °C) in distilled water.

A synthetic dyeing effluent (designated as SDE) was also prepared using DB, salt (NaCl) and auxiliary chemicals usually added to dyebaths in the industrial operations: a wetting agent (*Sera Wet C-AS*), which is anionic, a lubrificant agent (*Sera Lube M-CF*), non-ionic nature, and a sequestering agent, anionic (*Sera Quest M-PP*). The preparation of SDE was as follows [6]: 0.25 g of each one of the three auxiliary chemicals (wetting, lubrificant and sequestering) were dissolved in 250 mL warm distilled water; 150 mg of DB dye were added and the solution was heated to 100 °C; after 15 min, 2.5 g NaCl were added and the temperature was kept constant for 45 min, more; after cooling, the volume was made up to 1 L; this last dilution (250 mL to 1 L) simulates 3 washing baths (2 rinsing and 1 conditioning/softening baths) after dyeing. The whole procedure was based on a typical scheme used for cellulosic fibres dyeing with direct dyes and in other details provided by the dye supplier.

2.2. Sepiolite characterization

The sepiolite clay used as adsorbent is a commercial product with a grain size in the range 0.250–0.600 mm. According to its supplier it was composed by 80 wt.% sepiolite. Some properties of the clay (mean particle size, porosimetry, apparent and real densities, surface area by N_2 adsorption, cation exchange capacity, mineralogical and chemical analysis) were reported in a previous study [23]. Grain size distribution was obtained by laser diffraction, using water as dispersive medium. Mercury porosimetry (*Quantachrome, Poremaster 60*), helium picnometry (*Quantachrome*

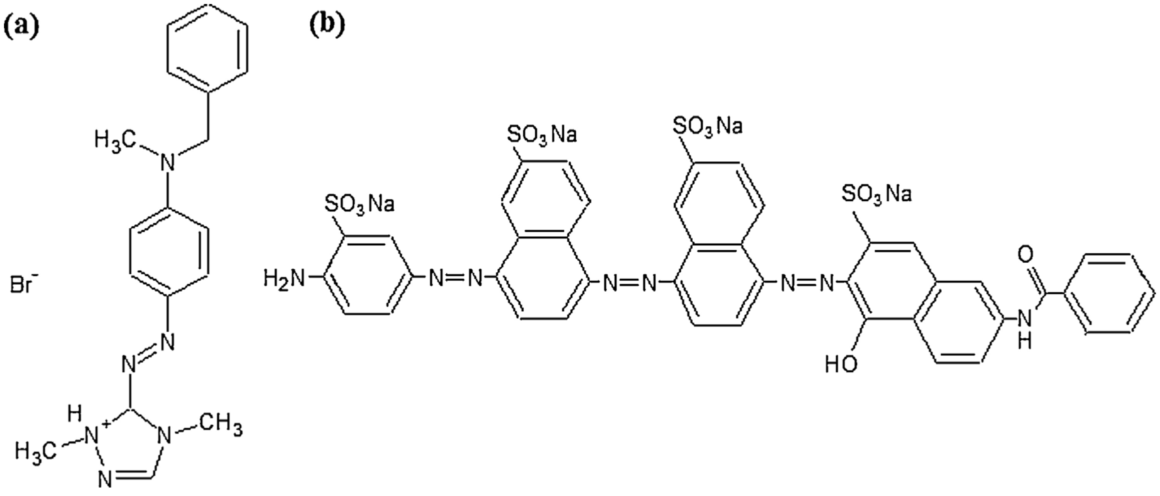

Fig. 1. Molecular structures of (a) Basic Red 46 and (b) Direct Blue 85 dyes.