Multi-parametric adsorption effects of the reactive dye removal with commercial activated carbons

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ABSTRACT

The aim of this study is to adsorptively evaluate the ability of some commercial activated carbons for the removal of a reactive dye from synthetic wastewaters. The model dye molecule used is Reactive Black 5 (RB5), while the activated carbon samples (fine powders after chopping) are: (i) Norit Darco 12 × 20 (DARCO), (ii) Norit R008 (R008), and (iii) Norit PK 1–3 (PK13). An extensive study about the influence of ionic strength to adsorption was also done, given that a crucial parameter in real dyeing wastewaters is the salinity. At first, pH-effect experiments showed the optimum pH-conditions (10). Then, kinetic (fitting to pseudo-first and -second order equations) and equilibrium experiments (fitting to Langmuir, Freundlich and Langmuir–Freundlich equations) indicated the crucial time-point in which the process ends and the maximum theoretical adsorption capacities (Q_m) for all carbon samples at 25 °C (348, 527, 394 mg/g for DARCO, R008, PK13, respectively). The increase of the ionic strength improved the capacity of each carbon sample used. Moreover, the effect of temperature on dye adsorption was tested and found to significantly enhance the removal of dye. The use of carbon samples in grain form (instead of fine powders) showed that the decrease of particle size improved the dye removal. The desorption ability of materials was low using pH-adjusted deionized water as eluant (pH = 2–10), while testing a surfactant as eluant at 25 °C (sodium dodecyl sulfate), higher desorption percentages were observed for all carbons, which further increased at high temperatures (85 °C: 83, 67, 42% for DARCO, PK13, R008, respectively). Based on the above adsorption results and with those exported from characterization techniques (BET, FTIR, SEM, Boehm titrations), some adsorption interactions were proposed.

1. Introduction

Wastewaters discharged from dye-houses can be one of the biggest contributors to aquatic pollution. The most studied dye classes, in dye bearing effluent treatment, are reactive and basic [1]. However, the larger amount of the dye loss from the dyeing process to the effluent is estimated to be 10–50% for reactive dyes [2]; therefore, it is necessary to firstly treat/remove these reactive dyes. Furthermore, wastewaters containing dyes are very difficult to be treated, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and stable to light, heat and oxidizing agents [3].

The dyeing process of cotton textiles using reactive dyes involves unit operations, such as (i) desizing, (ii) scouring, (iii) bleaching, (iv) dyeing, and (v) finishing [4]. The waste streams from each individual sub-operation are collected to an "equalization tank", where they are mixed and homogenized. In particular, the wastewater produced by the dyeing bath-reactor contains hydrolyzed reactive dyes, dyeing auxiliaries, and electrolytes (60–100 g/L of NaCl and Na_2CO_3). The latter are responsible for the high saline content of the wastewater, which exhibits

high pH values (10–11) [4]. In a typical dyeing procedure with reactive dyes, 0.6–0.8 kg NaCl, 30–60 g dyestuff, and 70–150 L water are required for the dyeing of 1 kg of cotton [5]. So, the large volume of colorized effluents, after the dyeing process, has to be treated in some manner. Additionally, the research on textile effluent decolorization has often been focused on reactive dyes for three main reasons [4]: (i) reactive dyes represent an increasing market share, because they are used to dye cotton fibers, which makes up about half of the world's fiber consumption; (ii) a large fraction, typically around 30% of the applied reactive dyes, is wasted due to the dye hydrolysis in alkaline dye bath; (iii) conventional wastewater treatment plants have a low removal efficiency for reactive and other anionic soluble dyes, which leads to colored waterways [5,6].

A typical effluent treatment is broadly classified into preliminary, primary, secondary, and tertiary stages [1,6,7]. The preliminary stage includes equalization and neutralization [7]. The primary stage involves screening, sedimentation, flotation, and flocculation. The secondary stage reduces the organic load and facilitate the physical/chemical separation (biological oxidation), while the tertiary stage is focused on decolorization [7]. In the latter stage, the adsorption onto activated carbon is broadly used to limit the concentration of color in effluents [8]. Adsorption has been applied either in a single mode, mainly for dyes

removal from synthetic wastewaters, or in a combinational mode for total cleaning of real dyeing wastewaters.

Among the technologies used for water and wastewater treatment, adsorption proved to be one of the most efficient separation methods for water purification. Numerous works have been recently published with primary goal which is the investigation of the removal of different pollutants (either in gas or liquid medium) using adsorbent materials [9–24]. In particular, adsorption was also found to be an effective treatment method for the removal of synthetic dyes from water and wastewaters that are toxic and cannot be efficiently decolorized by traditional methods. The release of dyes into environment constitutes an important proportion of water pollution [25]. The adsorption of synthetic dyes onto adsorbents is considered as a simple and economical method, especially when applied low-cost adsorbents [26–28]. The choice of the appropriate adsorbent materials is a very important issue. Carbon materials are well known for their use as excellent adsorbents [29,30].

In this study, some commercial carbon samples were tested as potential adsorbent materials for the removal of (one of the most widely-known dyestuffs existed in wastewaters) Reactive Black 5. The novelty of the present work is that many adsorption parameters affecting the process (i.e., pH of adsorption, initial dye concentration, temperature, ionic strength, particle size, contact time) were investigated along with the desorption potential of those materials (effect of pH on desorption). Some basic isotherm models (Langmuir, Freundlich, Langmuir–Freundlich) were used for fitting to equilibrium experimental results, in line with some kinetic equations (pseudo-first, -second order) for the respective of kinetic results.

2. Materials and methods

2.1. Carbon samples and model dye

Three carbon samples used in this study: (i) Norit Darco 12×20 (denoted as DARCO), (ii) Norit R008 (denoted as R008), and (iii) Norit PK 1–3 (denoted as PK13). The samples were purchased by Mead Westvaco (U.S.A.). The adsorbents were initially in granular form as purchased (DARCO, 1000 μm; R008, 800 μm; PK13, 1300 μm), but after chopping and sieving were used as fine powders (75–125 μm).

A commercial reactive dye (anionic and anthraquinonic) was used as a model dye molecule for adsorption experiments. The reactive dye used is Reactive Black 5 − C.I. 20505 (denoted as RB5, supplied by Kahafix), presents the following characteristics: $C_{26}H_{21}N_5Na_4O_{19}S_6$, MW = 991.82 g/mol, λ_{max} = 603 nm, purity = 55% w/w. The dye purity was taken into account for all calculations. The chemical structure of the dye used is given in Fig. 1.

2.2. Characterization techniques

Scanning electron microscopy (SEM) images were performed with an electron microscope (model Zeiss Supra 55 VP, Jena, Germany) equipped with an energy dispersive X-ray (EDX) Oxford ISIS 300 micro-analytical system. The accelerating voltage was 15.00 kV, while the scanning was performed in situ on a sample powder.

The FTIR spectra of the samples were taken with a Nicolet 560 (Thermo Fisher Scientific Inc., MA, USA) FTIR spectrometer. The spectra were recorded in transmission mode using potassium bromate wafers containing 0.5 wt.% of carbon. Pellets made of pure potassium bromate were used as the reference sample for background measurements. The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and are baseline corrected.

For the measurement of the surface pH of carbon samples, 0.4 g of dry carbon sample was added to 20 mL of water, and the suspension was stirred overnight to reach equilibrium. Then the pH of the solution was measured. This method provided information about the acidity or basicity of the material's surface.

The determination of surface functional groups was based on the Boehm titration method [31]. Aqueous solutions of NaHCO$_3$ (0.05 mol/L), Na$_2$CO$_3$ (0.05 mol/L), NaOH (0.10 mol/L), and HCl (0.10 mol/L) were prepared. 25 mL of these solutions was added to vials containing 0.5 g of adsorbents, let to be shaken (140 rpm) until equilibrium (24 h), and then filtered. Five blank solutions (without adsorbent) were also prepared. In this way, the number of the basic sites was calculated from the amount of HCl which reacted with adsorbent. The various free acidic groups were derived using the assumption that: (i) NaOH neutralized carboxyl, lactonic and phenolic groups; (ii) Na$_2$CO$_3$ neutralized carboxyl and lactonic groups, and (iii) NaHCO$_3$ neutralized only carboxyl groups. The excess of base or acid was then determined by back titration using NaOH (0.10 mol/L) and HCl (0.10 mol/L) solutions [32].

Nitrogen isotherms were measured using AS1Win (Quantachrome Instruments, FL, USA) at liquid N$_2$ temperature (77 K). The samples were degassed at 150 °C in a vacuum system at 10^{-4} Torr before the analysis. The specific surface area (S$_{BET}$) was calculated from the isotherm data using the Brunauer, Emmet and Teller (BET) model. The micropore volumes (V$_{mic}$) were obtained with the accumulative pore volume using the density functional theory (DFT) method. The total pore volumes (V$_{tot}$) were obtained from the volumes of nitrogen adsorbed at a relative pressure of 0.99 cm^3/g. The mesopore volumes (V$_{mes}$) were calculated by subtracting V$_{mic}$ from V$_{tot}$. The pore size distribution curves were also obtained using DFT method.

2.3. Adsorption experiments

2.3.1. Effect of pH on adsorption with varying ionic strength

The effect of pH was conducted by mixing 1 g/L of adsorbent with 20 mL of dye solution (C$_0$ = 500 mg/L). The pH value, ranging between 2 and 12, was kept constant throughout the adsorption process by micro-additions of HNO$_3$ (0.01 mol/L) or NaOH (0.01 mol/L). The pH adjustment of dye solutions in the presence of adsorbent was realized in order to study and understand the possible adsorption mechanisms in each particular pH condition. The dye removal is also occurred in free pH conditions (without readjustment to constant pH values), but in this way, it would be more difficult to examine the adsorption mechanism. The suspension was shaken for 24 h (agitation rate: N = 140 rpm) into a water bath to control the temperature at 25 °C (model Julabo SW-21C, Germany). All experiments were carried out at three ionic strength values (I = 0.001, 0.1, 1 M), adjusted by additions
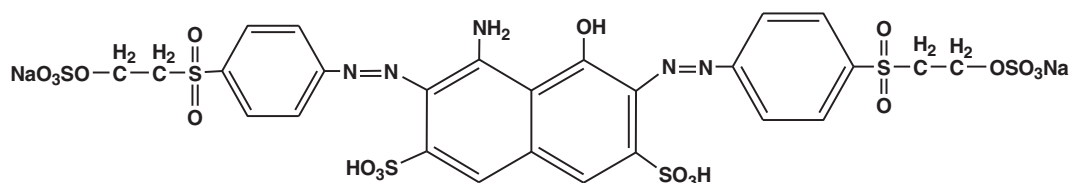

Fig. 1. Chemical structures of Reactive Black 5 (RB5).