



Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes



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ABSTRACT

Activated carbon from orange (*Citrus sinensis*) peel was developed through H_3PO_4 acid activation. Its ability as an adsorbent for the removal of two representative basic dyes (methylene blue and rhodamine B) from single and binary dyes solutions in batch and continuous modes was examined. The orange peel-based activated carbon presented a high specific surface area ($1090\text{ m}^2/\text{g}$), predominance of mesopores and acidic character. It also showed a high adsorption capacity for both dyes in batch and dynamic modes. Experimental equilibrium isotherms obtained from single-dye solutions fitted the Langmuir–Freundlich model, and those obtained from binary solutions were properly described by single and multi-component models. Breakthrough curves obtained from single-dye solutions exhibited a better removal performance for rhodamine B. Adsorption capacity at exhaustion time for this dye was 11% higher than for methylene blue. Additional experiments in dynamic conditions with a binary solution of both dyes pointed to adsorption competition for the active sites of the developed carbon. Breakthrough curves were adequately represented by a modified two-parameter model.

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1. Introduction

Among wastewaters treatment methods, adsorption using activated carbons (ACs) has been found superior to others in terms of initial costs and simplicity of design and operation (Wawrzkiwicz and Hubicki, 2009). ACs are successfully proven adsorbents employed nowadays for the full-scale treatment of wastewaters, mainly for its efficiency and ease of implementation (Benadjemia et al., 2011). However, because of the elevated cost of production, available agricultural solid wastes are being intensively investigated for the production of low cost effective ACs. The conversion of waste materials into ACs adds economic value, helps reduce the cost of waste disposal, and provides a potentially less expensive alternative to the existing commercial samples

(Rafatullah et al., 2010). Orange peels are one of these valuable waste materials discarded from juice industry. Since world orange production is estimated in more than 60 millions tons (Siles López et al., 2010) and a significant fraction is destined to industrialization, land space occupation and pollution with phenolic compounds due to dumping of the waste, are becoming problematic (El Nemr et al., 2009).

In addition, watercourses are threatened by a large number of toxic compounds. Among them, about 10% of the hundreds of thousands tons of dyes produced annually worldwide may be found in wastewaters and their complex aromatic molecular structures make them very stable and difficult to biodegrade (Deniz et al., 2011; Rodríguez Couto, 2009). Numerous studies are focused on adsorption of dyes from single-component systems (Dutta et al., 2011; Hao et al., 2010). However, effluents are a mixture of several contaminants, and available data on possible enhancing or inhibitory effects on the adsorption of dyes in a mixed system is limited (Janaki et al., 2012). Moreover, sometimes the data acquired in batch mode are not applicable to treatment systems where contact time is not sufficient to attain equilibrium, and then continuous adsorption studies are needed (Lodeiro et al., 2006). So far, only

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few studies have focused on the conversion of orange peels into ACs and their ability to remove dyes (El Nemr et al., 2009; Foo and Hameed, 2012), and there is no precedent of any orange peel-based AC investigated as an adsorbent for mixtures of dyes in batch and continuous modes.

Within this framework, the present work focuses on the development of an activated carbon using orange peel through chemical activation with H_3PO_4 acid and the examination of the feasibility of using it as an adsorbent for the removal of two representative basic dyes, methylene blue (MB) and rhodamine B (RhB), from single and binary solutions in batch and continuous modes. This is a closer approach to real wastewater since it considers the simultaneous co-existence of two dyes. The physicochemical and textural characteristics of the developed carbon were evaluated and compared with those of the precursor. The effects of main operational parameters were examined to optimize removal process variables. Kinetic and equilibrium adsorption parameters were obtained from the application of mathematical models to experimental data. Finally, continuous removal of both dyes was assessed through experiments in an up-flow column.

2. Materials and methods

2.1. Materials

Oranges (*Citrus sinensis*) were purchased from a local fruit market, washed with tap water to eliminate dust and other residues and peeled. The orange peels were cut in small pieces and dried at $60^\circ C$. The dried samples were then crushed, milled and further rinsed with warm water, dried again and finally screen-sieved. The precursor material obtained is hereafter abbreviated as OPP. The fraction of particle diameter between 500 and 1000 μm was selected for the preparation of the activated carbon.

Two basic dyes of analytical grade were used for the adsorption experiments: methylene blue (basic blue 9, C.I. 52015, M.W. 373.91 g/mol) purchased from Carlo Erba[®], and rhodamine B (basic violet 10, C.I. 45170, M.W. 479.02 g/mol), purchased from Sigma-Aldrich[®]. Analytical grade H_3PO_4 acid was purchased from Biopack[®].

2.2. Preparation of the activated carbon

An OPP sample was mixed with a 50 wt.% H_3PO_4 acid solution, in a 2:1 acid/precursor weight ratio, and allowed to soak for 2 h at $110^\circ C$. Afterwards, the impregnated sample was placed in a stainless steel fixed-bed reactor heated by an electrical furnace. The temperature was raised from room temperature up to $475^\circ C$ at a heating rate of $3^\circ C/min$ and held for 0.5 h. Selection of the former conditions was based on previous findings for other precursors (Basso et al., 2002; de Celis et al., 2009). After cooling to room temperature, the sample was soaked in an alkaline solution for 10 min and subsequently rinsed with hot water until a neutral pH was attained. Finally, distilled water was used to complete the rinse. A test using a lead nitrate solution was performed to check for any residual, free, or loosely bound phosphate which could affect further uptake assays (Basso et al., 2002). The sample was then dried in an oven to constant weight, and the yield was evaluated. The developed activated carbon is hereafter abbreviated as OPAC. Yields of 33% were attained.

2.3. Characterization of OPP and OPAC

The fraction of particle diameter between 250 and 500 μm was selected for the characterization of the precursor and the adsorbent. Proximate analysis was performed by thermogravimetric analysis (TA Instruments SDT Q600), according to the American Society of

Testing and Materials' (ASTM) 5142 standards. An automatic elemental analyzer (Carlo Erba model EA 1108) was used to assess their elemental composition.

The total and individual amounts of acidic/polar oxygen functional groups (TOFGs), i.e. carbonyls, phenols, lactones, and carboxyl groups, on the surface of the developed OPAC were determined by titration, following a modified procedure based on Boehm's method (de Celis et al., 2009), and employing solutions of sodium ethoxide, sodium hydroxide and sodium bicarbonate. Likewise, total basic surface groups (TBGs) were determined, following the procedure described in Nunell et al. (2012) and employing a HCl solution. Average values expressed as milliequivalents per gram of sample are reported. Identification of surface functionalities of OPP and OPAC was complementary conducted by Fourier transformed infrared (FT-IR) spectroscopy. The spectra were recorded by transmission method, using a Perkin-Elmer IR Spectrum BXII spectrometer within the range $600\text{--}4000\text{ cm}^{-1}$. Each sample was ground with KBr at an approximate ratio of 1:200 and the resulting mixture was then pressed. The pH of point of zero charge (pH_{pzc}) for OPAC was assessed following the procedure depicted in detail in our previous study (Fernandez et al., 2010).

N_2 adsorption-desorption isotherms at $-196^\circ C$ for OPP and OPAC were determined with an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Prior to gas adsorption measurements, the dried samples were outgassed at $60^\circ C$ (for OPP) and $120^\circ C$ (for OPAC) overnight. Textural properties were assessed from the isotherms, according to conventional procedures (Nunell et al., 2012). The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) was determined by the standard BET procedure and total pore volume (V_t) was estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95 ($p/p_0 = 0.95$). The mean pore width (W) was calculated from $W = 4V_t/S_{BET}$. Pore size distribution (PSD) of the activated carbon was calculated from N_2 adsorption data using the DFT Plus Software (Micromeritics Instrument Corporation), based on the non-local density functional theory (Puziy et al., 2007).

Scanning electron microscopy (SEM) was performed in a Zeiss Supra 40 microscope equipped with a field emission gun and coupled with an energy dispersive spectrometer (EDS, Oxford-instrument Inca x-sight). The images were taken with an in-lens detector and 3 kV acceleration voltages. The samples were placed on an aluminum holder, supported on conductive carbon tape and sputter coated.

2.4. Batch experiments

Stock solutions of 2.1 mmol/L were prepared by dissolving the necessary amount of methylene blue and rhodamine B in distilled water and diluted to obtain the desired concentrations of the dyes. Adsorption experiments were carried out using capped Erlenmeyer flasks in a batch thermostated system (Lauda Ecoline E200) at $20 \pm 0.5^\circ C$, under a wrist-action shaker agitation at a constant speed of 250 rpm up to equilibrium. Afterwards, all samples were centrifuged for 10 min at 5000 rpm and the concentration of each dye was calculated from the measured absorbance in the supernatant at their corresponding maximum absorption wavelength ($\lambda_{max}MB = 663\text{ nm}$ and $\lambda_{max}RhB = 553\text{ nm}$) by means of an UV-vis spectrophotometer (Shimadzu Model UV mini 1240). The fraction of particle diameter between 250 and 500 μm was selected for most batch experiments, with the exception of kinetic experiments, where the fraction between 105 and 250 μm was used, to avoid external and intraparticle mass transfer resistances.

The pH effect on dyes adsorption was studied in the range 2–10. Dyes solutions of alkaline pH were prepared using buffers because it was difficult to maintain these pH values throughout the experiments duration. Solutions of the remaining pH were prepared with distilled water and adjusted with HCl and NaOH solutions. Amounts

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