



Rhodamine B removal with activated carbons obtained from lignocellulosic waste



Viviane da Silva Lacerda ^a, Juan B. López-Sotelo ^a, Adriana Correa-Guimarães ^a, Salvador Hernández-Navarro ^a, Mercedes Sánchez-Báscones ^a, Luis M. Navas-Gracia ^a, Pablo Martín-Ramos ^b, Jesús Martín-Gil ^{a,*}

^a Department of Agricultural and Forestry Engineering, ETSIIAA, Universidad de Valladolid, Avenida de Madrid 44, 34004 Palencia, Spain

^b Department of Agricultural and Environmental Sciences, Higher Polytechnic School of Huesca, Universidad de Zaragoza, Carretera de Cuarte s/n, 22071 Huesca, Spain

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ABSTRACT

By-products from the wax production process from carnauba palm (leaves), from the extraction of oil from macauba seeds (endocarp) and from pine nut production (shell) have been assessed for activated carbon production, using H_3PO_4 or $CaCl_2$ for their chemical activation. The resulting activated charcoals have been thoroughly characterized by elemental and thermal analysis, X-ray diffraction, infrared spectroscopy, electron scanning microscopy and N_2 adsorption behavior. Subsequently, their adsorption capacity for the removal of rhodamine B (RhB) from aqueous solutions has been evaluated by studying different parameters: contact time, pH, adsorbent dose, initial dye concentration and solution temperature. The adsorption of RhB followed Freundlich's model in all cases. Kinetic studies indicate that the pseudo-second order model can be used for describing the dynamics of the adsorption process. Thermodynamic parameters have also been evaluated, indicating its endothermic and spontaneous nature. Finally, a preliminary analysis of the impact of cellulose content in the carbon precursor materials has been conducted, by using a mixture of native cellulose with one of the lignocellulosic materials.

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1. Introduction

Synthetic dyes are widely used in industries, producing a large amount of toxic, carcinogenic, mutagenic, bio-accumulative wastewaters that pollute the environment (Chen et al., 2010) and which have been deemed as one of the most important groups of contaminants for the aquatic environment (Hosseini et al., 2011). Dyes are difficult to remove by conventional wastewater purification treatments due to their high stability against light, temperature, chemical and microbial attacks (Forgacs et al., 2004). Wastewater from industries also are contaminated by heavy metals (Lo et al., 2012), causing severe poisoning due to their high solubility in water and their non-biodegradability (Zaini et al., 2010). One of the most widely used products for the removal of these pollutants are activated carbons (activated charcoals), which can be produced from agricultural residues

such as pecan nut shell (Bansode et al., 2004; Klasson et al., 2009; Ng et al., 2003), leather waste (Kong et al., 2013), olive-waste cake (Baccar et al., 2009), grass clippings, horse manure (Hao et al., 2013), rice husk waste (de Luna et al., 2013), etc.

The adsorption technique is used for the treatment of industrial effluents, and activated carbon is extensively used for the removal of many pollutants, but it has the disadvantage of having a high associated cost. Consequently, other low-cost materials have been proposed as alternatives, in particular residual biomass, which is a natural biodegradable renewable product, with a minimum associated cost and which also has good adsorption properties for contaminants, either metals or chemical compounds (Paraskeva et al., 2008).

The adsorption involves the separation of a substance, followed by its accumulation or concentration on the surface of another material (Metcalf and Eddy, 2003). Activated charcoal of plant origin is a versatile adsorbent of great economic interest for the treatment of water, either for human consumption or for industrial purposes.

The aim of this research has been to find an efficient way to

* Corresponding author.

E-mail address: jesusmartingil@gmail.com (J. Martín-Gil).

produce, characterize and use activated charcoals obtained from three little exploited lignocellulosic waste materials (from *Copernicia prunifera*, *Acrocomia aculeata* and *Pinus pinea*) for the adsorption of contaminants in wastewaters, taking Rhodamine-B (RhB) as a representative -and particularly harmful- example of industrial pollutant dye. The effect of impregnation of the raw materials with H_3PO_4 and $CaCl_2$ has been assessed, together with the impact of variations of the pH, concentration of adsorbate, contact time, temperature and adsorbent dose on the efficiency of the adsorption process. Rhodamine-B adsorption mechanisms have been analyzed through isotherms, kinetic and thermodynamic studies. Moreover, the effect of the cellulose content in the precursor materials on the RhB removal capability of the resulting activated charcoals has been evaluated by its artificial increase with native cellulose for the first time.

2. Materials and methods

2.1. Precursor materials

Carnauba palm (*C. prunifera*) leaves from Ceara (Brazil), macauba palm (*A. aculeata*) endocarp from Minas Gerais (Brazil) and stone pine (*P. pinea*) nut shells from Valladolid (Spain) have been selected as precursor lignocellulosic materials (da Silva Lacerda et al., 2015). Commercial native cellulose was supplied by Merck. Phosphoric acid (H_3PO_4 , 85%) and hydrochloric acid (HCl, 37%) were purchased from Panreac, and calcium chloride ($CaCl_2$, anhydrous, >93%) from Sigma Aldrich.

2.2. Activated carbon preparation

The chemical activation of the lignocellulosic raw materials was carried out using phosphoric acid and calcium chloride. Prior to the impregnation of the materials, they were washed with deionized water until constant pH and then were grounded on a Retsch ZM-100 ultra centrifugal mill to a particle size <0.25 mm. Subsequently, the materials were impregnated with solutions of phosphoric acid (1 M) and calcium chloride (1 M), using 8 g of each lignocellulosic product in 100 mL of the respective solutions (H_3PO_4 -1 M and $CaCl_2$ -1 M) for 24 h. After impregnation, the samples were filtered and dried at room temperature for 24 h. The carbonization of the materials was conducted in a Mufla Digital oven mod. 10-PR/300 at 500 °C for 1 h under N_2 atmosphere. The materials resulting from carbonization were washed with 50 mL of hydrochloric acid (1 M) for 1 h and sonicated for 10 min in a JP Selecta ultrasonic cleaning bath, and then filtered and washed with deionized water until chlorides complete elimination and constant pH were attained. The charcoals were finally dried to remove all moisture. Aforementioned washing process is essential in order to remove the chemical activating agents, allowing higher porosity (Peláez-Cid and Teutli-León, 2012).

2.3. Physico-chemical characteristics of the activated carbons

The behavior of the impregnated materials against pyrolysis was studied in a Mettler Toledo TGA/SDTA851e/SF/1100 thermal analyzer, by heating the samples from 25 to 830 °C at a 25 °C/min rate under nitrogen atmosphere. The sample weights were in the 9.5–10.5 mg range, each of them determined with 0.01 mg precision.

C, H and N contents were measured using a Leco CHN-600 Elemental Analyzer. Since ash and metal contents are low for these lignocellulosic materials, the oxygen content was calculated by subtraction, following a procedure analogous to that of Pastor-Villegas et al. (2006).

The content of cellulose, hemicellulose and lignin was determined for each of the precursor materials as follows: the insoluble lignin content was calculated according to ANSI/ASTM standard (ANSI and ASTM, 1977) and holocellulose (hemicellulose + cellulose) was obtained after delignification of the sample and its content was determined using the technique described by Browning (1967). Cellulose content was determined according to ANSI/ASTM procedure (ANSI and ASTM, 1977) and hemicellulose content was then calculated by subtraction of cellulose content to that of holocellulose.

Structural characterization of the charcoals by X-ray powder diffraction was carried out in a Bruker D8 Advance Bragg-Brentano diffractometer, in reflection geometry. The diffractograms were recorded with 2θ sweep angles in the 5–70° range at 0.02 (2θ /sec) speed with 2 s exposure time.

The functional groups present on the surface were determined by infrared spectroscopy using a Thermo Nicolet 380 FT-IR apparatus equipped with a Smart Orbit Diamond ATR system.

The pore structure of the samples was characterized by nitrogen adsorption-desorption at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to the analysis, samples were degassed for 2 h under vacuum at 393 K.

The surface morphology was studied by scanning electron microscopy (SEM) in a FEI Quanta 200F apparatus.

2.4. RhB adsorption assays

Batch adsorption experiments were conducted to investigate the adsorption of Rhodamine B on the various activated carbons. All determinations were performed in triplicate biological replications, and the reported values correspond to the average.

To analyze the effect of pH on RhB adsorption, experiments were carried out at initial pH values ranging from 2 to 10. The initial pH was controlled by the addition of dilute HCl or NaOH solutions. The effect of the dose of adsorbent was studied by varying the amount of carbon in the solution (from 2 to 8 g/L). The influence of contact time was assessed by using the same dye concentration and changing the contact time from 5 to 240 min. The impact of the initial dye concentration was determined by isotherms at 25, 35 and 45 °C, varying the initial dye concentrations from 65 to 140 mg/L while keeping the dose of adsorbent and the contact time fixed. Finally, with a view to determining to what extent the amount of cellulose in the precursor materials affected the RhB adsorption capacity, a preliminary study has been conducted by mixing different amounts of native cellulose (0 wt.%, 20 wt.% and 50 wt.%) with one of the lignocellulosic materials (pine nut shell) and comparing the percentage of removal of RhB for each the resulting activated charcoals. The aim of adding such native cellulose was to artificially increase the cellulose content prior to the activation phase (with H_3PO_4).

Rhodamine B concentrations in the solution before and after adsorption were determined with a Hitachi U-2001 UV-vis spectrophotometer at 552 nm. The amount adsorbed per unit mass of biosorbent (mg/g) is calculated using the following equation (Eq. (1)):

$$q_t = [V(C_0 - C_t)]/m \quad (1)$$

where C_0 (mg/L) is the initial concentration, C_t (mg/L) is the concentration in the liquid phase at time t , V (L) the volume of the solution and m (g) the mass of adsorbent. In equilibrium conditions, $q_t = q_e$ and $C_t = C_e$.

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