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Removal of dyes by lignocellulose adsorbents originating from biodiesel production

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ABSTRACT

In this study, use was made of tucumã cake, *in natura* (TCN) and thermally treated (TCT), as potential alternative adsorbents for the adsorption of cationic and anionic dyes. The effects of the parameters: contact time, adsorbent: adsorbate mass ratio, and initial concentration of dye were analyzed. The adsorption isotherms were established from optimized adsorption parameters. The best conditions for adsorption were: equilibrium time of 7 h, concentration of 25 mg L^{-1} and ratio of 1:200 for the methylene blue dye; and pH 6.5, concentration of 25 mg L^{-1} and ratio of 1:200 for the congo red dye. The adsorption process was best represented by the Dubinin–Radushkevich and Sips isotherms. The kinetics of adsorption of the dyes were best described by the pseudo-second-order kinetic and Elovich models. TCT showed the best maximum adsorption capacity (Q_m) for the methylene blue dye (63.92 mg g^{-1}).

1. Introduction

Color is one of the most easily detected properties of an effluent and the most obvious indicator of water pollution, and the presence of dyes in effluents is of serious concern, due to the adverse effects that they can cause to different forms of life [1].

The use of dyes occurs in different industrial sectors such as: textiles, leather, cosmetics, paper, plastic and rubber, resulting in a profuse production of effluents with highly toxic components and serious environmental impact. As the great majority of dyes are of synthetic origin, their structures display aromatic rings and azo groups, which are only poorly susceptible to oxidation processes and thus non-biodegradable, necessitating the use of other methods for the removal of these components of industrial effluent [2].

Among the various processes used to treat water contaminated by dyes, adsorption may be considered the most efficient, and therefore is widely used in industry. The majority of commercial systems currently use activated carbon as adsorbent to remove dyes in wastewaters because of its excellent adsorption ability. However, although activated carbon is a preferred adsorbent and, its widespread use is restricted due to its high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents [3].

The use of low-cost adsorptive materials has brought about increasing interest in the removal of dyes in aqueous solution. Among the very varied types of natural materials used in the adsorption process, various residues stemming from industry or from agriculture may be mentioned [1,4–6], and also clays [7,8].

In this process, the use of agro-industrial wastes arouses great interest, because they are constituted of macromolecules such as lignin, cellulose, hemicelluloses and compounds resulting from the secondary metabolism of plant organisms, which possess adsorptive sites, such as carbonyl, carboxyl, amine and hydroxyl groups, capable of adsorbing the most varied pollutants [9]. In the literature, several studies describe the use of these alternative adsorbents, and among them can be cited: leaves of *Azadirachta indica* [10], sawdust [11], corncob [12], cupuassu shell [13],*Carica* papaya seeds [14], Formosa papaya seed [15], mustard husk [16], oil palm fibers [17], sugarcane bagasse [18], *Jatropha* oil cake [18,19], as well as other lignocellulose materials. The agro-industrial wastes are renewable and available in large amounts. These wastes are good adsorbents because they are usually used without or with a minimum of processing (washing,

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drying, grinding) and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment [1].

In this context, combining the need to reduce commercial adsorbent costs with the need to employ residues of vegetable origin as adsorbents for the removal of pollutants from industrial effluents, the object of this research was to use tucumã cake (lignocellulose material) as adsorbent materials for the model molecules of methylene blue (MB) and congo red (CR) in aqueous medium. The equilibrium and kinetic data of the adsorption process of the dye onto the adsorbents was also studied.

2. Material and methods

2.1. Preparation of dye solutions and adsorbent

The dilute solutions of dyes employed in the adsorption studies were prepared from stock solutions containing 5000 mg L^{-1} of either methylene blue ($C_{16}H_{18}ClN_3S$; 3.7-*bis*(dimethylamino)-phenothiazin-5-ium chloride; λ_{max} = 668 nm) and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$; sodium 3.3′-(1E.1′E)-biphenyl-4.4′-diylbis(diazene-2.1-diyl)*bis*(4-aminonaphthalene-1-sulfonate); λ_{max} = 500 nm). The natural pH values of the dye solutions were approximately 5.0 (MB) and 6.5 (CR), and these were adjusted (where necessary) by the addition of either 0.02 mol L^{-1} potassium hydroxide or 0.02 mol L^{-1} hydrochloric acid solutions The three-dimensional structures of the dyes studied were optimized by Gaussian 09 program and are presented in Fig. 1.

The lignocellulose materials were dried for 24 h in an air oven at 40 °C, reduced to a powder and sieved (40–60 mesh) to produce the tucumã cake *in natura* (TCN). A portion of TCN (50 g) was heated at 130 °C for 24 h, cooked in 300 mL of type II water for 2 h to remove soluble phenolic compounds, washed with type II water, and finally dried for 3 h in an air oven at 90 °C to produce the tucumã cake thermally treated (TCT) [20].

2.2. Characterization of adsorbents

The percentages of C, H, N, S and O (by difference) in TCN was determined by an Elementar Analyse system vario Micro cube™ (Germany). Thermogravimetric analyses were performed using a Shimadzu model DTG-60AH thermomechanical analyzer and were carried out under a nitrogen atmosphere in the temperature range of 25–900 °C at a heating rate of 10 °C min^{-1}. The Fourier transform infrared spectra (FTIR) of adsorbents (in the form of KBr pellets) were measured using a Bruker series Vertex 70V (Germany) spectrometer in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. Microscopic observations and electron micrographs were made using a Nano Technology Systems model Evo® 40 VP SEM (Germany). The N_2 adsorption/desorption isotherms were obtained at −196 °C in an Autosorb 1 Quantachrome apparatus (USA). The sample was pretreated at 200 °C under flowing nitrogen for 3 h. The pore size distribution was determined using the BJH method. The specific surface area and external area were determined using the BET equation and t-plot method, respectively. Zeta potential was measured using a Zeta Meter 3.0+, model ZM3-D-G (Zeta Meter Inc., USA). The suspensions of the adsorbent, ground before hand to less than 37 μm, were sedimented/conditioned at a temperature of 22 °C for 2 h, at the selected pH, in 250 mL measuring cylinders with the addition of a 2 mmol L^{-1} solution of $NaNO_3$, used as an indifferent electrolyte. The applied tension varied in the range 75–200 mV. The average of 20 measurements was taken as representing the measured potential.

2.3. Adsorption experiments

To evaluate the efficiency of the TCN and TCT in removing dye, batch experiments were performed in which different amounts of biosorbent samples were added to 10 mL aliquots of dye solution and the resulting mixtures maintained at room temperature (25 ± 1 °C) on an orbital shaker at 100 rpm (Nova Ética, mod. 109,

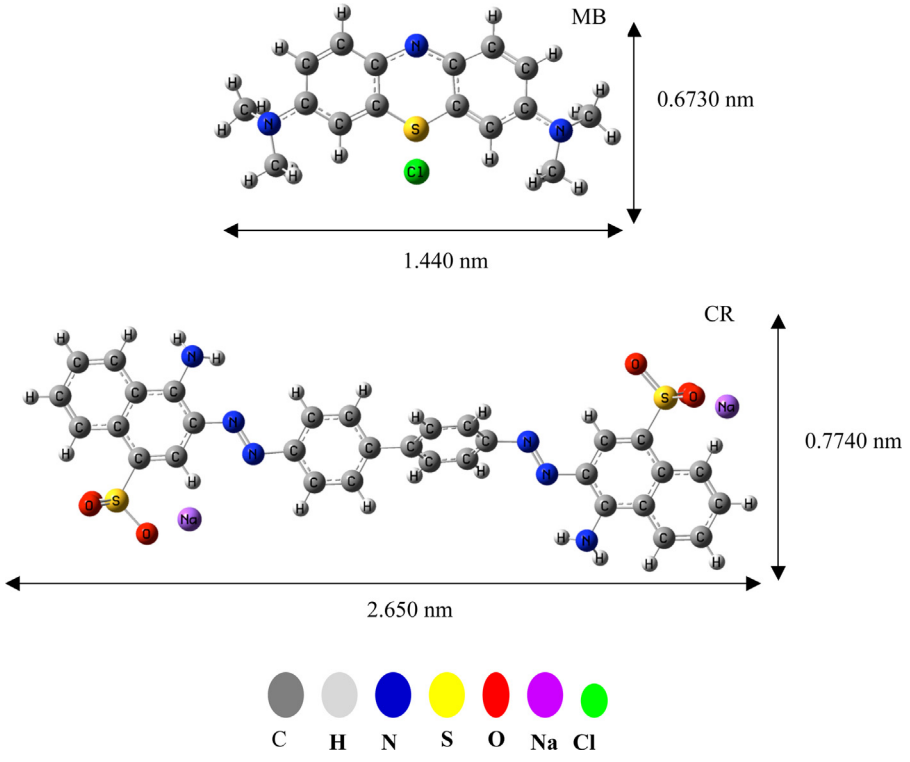

Fig. 1. Optimized three-dimensional structures of MB (a) and CR (b). The dimensions of the chemical molecule were calculated using Gaussian 09 program.