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Magnetic modification of microporous carbon for dye adsorption



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ABSTRACT

In this study, impregnation of microporous activated carbon with magnetite was achieved by co-precipitation of iron salts onto activated carbon. The evaluation of the adsorption ability of this material was examined using the anionic dye Reactive Black 5 as model dye pollutant (adsorbate). The effect of pH, ionic strength, contact time and initial dye concentration were also studied. It was found that high pH and high ionic strength favor the adsorption of Reactive Black 5. The adsorption kinetics and isotherms were well fitted by the fractal BS model and Langmuir model, respectively. The impregnation with magnetite decreases the adsorption capacity of activated carbon. Thermal re-activation of dye-loaded activated carbons was also succeeded. The characterization of the magnetic carbons was investigated by various techniques (SEM/EDAX, VSM, BET, FTIR, XRD, DTG) revealing many possible interactions in the carbon-dye system.

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1. Introduction

Dyes are important water pollutants which are generally present in the effluents of textile and dye manufacturing industries. The dye effluent is considered to be highly toxic to the aquatic biota and affect the symbiotic process [1]. Among the numerous techniques of dye removal from aqueous solutions, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials. If the adsorption system is designed correctly it will produce a high-quality treated effluent [2].

Currently, most commercial systems use activated carbon (AC) as sorbent to remove dyes from wastewaters because of its excellent adsorption ability. There are two common adsorption designs for wastewater treatment, namely, stirred-batch and fixed-bed adsorber systems. The former is certainly simple and allowed to reach equilibrium quickly but with solid/liquid separation problems. In contrast, the latter involves external and internal mass transfer difficulties [3]. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies [4,5]. Although activated carbon is a preferred sorbent, its widespread use is restricted due to high purchase and operational cost [6].

In order to decrease the purchase cost of activated carbon, attempts have been made to exploit low-value biomass to produce activated carbon at 600 \$/t [7]. In the past few years, magnetic

sorbents have emerged as a new generation of materials for environmental decontamination since magnetic separation simply involves applying an external magnetic field to extract the adsorbents. Compared with traditional methods, such as filtration, centrifugation or gravitational separation, magnetic separation requires less energy and less operational costs [8–11].

Several methods have been developed to combine together activated carbon and magnetic particles to produce magnetic composites such as impregnation, ball milling, and chemical co-precipitation. Among these methods, chemical co-precipitation is the most promising because it is simple and no special chemicals and procedures are demanded [8–11].

In order to describe activated carbon and especially its adsorption properties, two main concepts are important to be considered: porous morphology (surface area and porous structure) and surface chemistry [12]. It is well known that porous structure determines adsorption capacity, which depends on accessibility of the adsorbate molecules into pores and consequently on the size of pores and of adsorbate [4]. Thus, whereas an essentially microporous carbon could be adequate for the adsorption of gases and vapors, a well-developed meso- and macroporosity is required to accelerate the kinetics of the adsorption process or for the adsorption of larger molecules such as found in some solutions [13].

However, it has been shown that the role of surface chemistry in adsorption of inorganic compounds from aqueous solution is higher than porosity. Chemistry of surface strongly influences hydrophobicity, electronic density of graphene layers and type of interaction of AC with adsorbate because adsorbate molecules may interact with some surface functional groups [14].

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The magnetic mesoporous carbons are highly attractive in adsorption processes. However, their multi-step synthesis via hard or soft-templating is time consuming, laborious and high cost [15]. So, the adsorption features of magnetic microporous activated carbon still remain a challenge. In this regard, the effect of magnetic modification of a commercial microporous activated carbon was realized for the treatment of a simulated reactive dye effluent (Reactive Black 5). Activated carbon/iron oxide magnetic composites were characterized by SEM/EDAX, FTIR, XRD, DTA, DTG and VSM magnetization. The adsorption behavior of the composite materials was performed in batch mode, studying the effect of pH, contact time, background electrolyte, temperature and regeneration of dye-loaded carbon.

2. Materials and methods

2.1. Materials

The activated carbon used for the magnetite impregnation was a coconut-shell-based microporous carbon namely S208, which is manufactured by Calgon Carbon Corporation. This initial non-modified sample is denoted hereafter as S. The dye used as target molecule for the adsorption evaluation of carbon was the Reactive Black 5 – C.I. 20505 (commercial reactive dye with anionic anthraquinonic groups) and abbreviated hereafter as RB5. It was supplied by Kahafix and presented the following properties: $C_{26}H_{21}N_5Na_4O_{19}S_6$; M.W. = 991.82 g/mol, $\lambda_{max} = 603$ nm, purity = 55% w/w. Sodium hydroxide (NaOH), ammonia solution (NH₄OH), iron (III) chloride (FeCl₃·6H₂O) and iron (II) chloride (FeCl₂·4H₂O) were of analytical grade and purchased from Sigma–Aldrich.

2.2. Impregnation of activated carbon

The impregnation of the activated carbon with magnetite was achieved by co-precipitation of the two salts of iron (FeCl₃·6H₂O and FeCl₂·4H₂O) on activated carbon. The agents of precipitation were NaOH (1 M) and NH₄OH (28% v/v). Briefly, in a typical synthesis procedure of magnetite nanoparticles, 4 g of activated carbon was dispersed in 100 mL of deionized water. 0.825 g of FeCl₂·4H₂O and 2.375 g of FeCl₃·6H₂O were added and the solution was kept at 60 °C under nitrogen atmosphere by stirring at 400 rpm for 1 h. The resulting solution was precipitated at 60 °C by adding dropwise (under vigorous stirring in nitrogen atmosphere) until the pH of the solution reached the value of 10. The suspension was heated at 90 °C and kept at this temperature for 1 h under continuous stirring. It was then filtrated, washed with distilled water until neutral pH and then with ethanol and finally freeze-dried. The magnetic activated carbon prepared after NaOH precipitation was denoted as Sm, while the other one after NH₄OH precipitation was denoted as Sma. The carbon samples after RB5 adsorption are denoted with the abbreviation “RB5” in parenthesis at the end of their assignment.

2.3. Adsorbents characterization

X-ray powder diffraction (XRD) patterns were recorded with a Cu K α radiation for crystalline phase identification (model Richard Seifert 3003 TT, Ahrensburg, Germany). The sample was scanned from 20° to 80°.

The magnetic property was measured on a vibrating sample magnetometer (VSM) (Oxford Instruments, Oxford, UK) at room temperature.

Scanning electron microscopy (SEM) images were performed with electron microscope (model Zeiss Supra 55 VP, Jena, Germany). The accelerating voltage was 15.00 kV and the scanning was performed in situ on a sample powder. EDAX analysis was

done at magnification 10 K and led to the maps of elements. All the studied surfaces were coated with carbon black to avoid charging under the electron beam.

Textural characteristics were measured from nitrogen adsorption using AS1Win (Quantachrome Instruments, FL, USA) at liquid N₂ 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 Density Functional Theory (DFT) method. The total pore volumes (V_{tot}) were obtained from the volumes of nitrogen adsorbed at a relative pressure of 0.95 cm³/g. The mesopore volumes (V_{meso}) were calculated by subtracting V_{mic} from V_{tot} . The pore size distribution curves were also obtained using DFT method.

Thermal analysis was carried out using a TA Instrument thermal analyzer (SDT) (Q500 model, TA Instruments, New York, USA) at a heating rate of 10 K/min, and a flow rate of nitrogen atmosphere equal to 100 mL/min. Approximately 25 mg of sample was used for each measurement. The FT-IR spectra of carbons before (non-loaded) and after adsorption (dye-loaded) were obtained (model FTIR-2000, Perkin Elmer, Dresden, Germany) in the range of 4000–500 cm⁻¹ using KBr pellets. 2 cm⁻¹ was the resolution for each spectrum with 32 co-added scans. The spectra presented are baseline corrected and converted to the transmittance mode.

To find the iron loading on carbon, 0.2 g of carbon was ashed at 600 °C and then digested with 25 mL of concentrated hydrochloric acid. The digestion solutions were analyzed for iron by a Perkin Elmer A Analyst 400 Atomic Absorption Spectrophotometer. For the surface pH measurements of carbons, 0.4 g of dry sample were added to 20 mL of deionized water, and the suspension was stirred overnight to reach equilibrium. Then, the pH of the solution was measured.

2.4. Adsorption–regeneration experiments

The adsorption experiments were conducted in 50 mL conical flasks, in triplicate. The mass of adsorbents was 0.02 g, the volume of solution 25 mL and the shaking rate 160 rpm.

In the case of pH-effect experiments, the adjustment of solutions was done with micro-additions of acid (0.01 M HCl) or base (0.01 M NaOH) at 25 °C as fixed temperature for 50 h (contact time) with 1 M NaCl (ionic strength). After finding the optimum pH value (pH = 10), equilibrium experiments were carried out at 25, 45, 65 °C varying the initial RB5 concentration (0–100 mg/L), but keeping constant all other parameters. The resulted experimental data were fitted to Langmuir (Eq. (1)) [16] and Freundlich (Eq. (2)) [17] isotherm equations:

$$Q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e} \quad (1)$$

$$Q_e = K_F C_e^{1/n} \quad (2)$$

where Q_e (mg/g) is the equilibrium dye concentration in the solid phase; Q_{max} (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F (mg^{1-1/n} · L^{1/n}/g) is the Freundlich constant representing the adsorption capacity, n (-) is the constant depicting the adsorption intensity.

The amount of total dye uptake at equilibrium Q_e (mg/g) was calculated using the mass balance equation where C_e (mg/L) is the residual dye concentration (Eq. (3)):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (3)$$

The effect of ionic strength on RB5 adsorption was determined performing the equilibrium experiments as described but using 3 values of ionic strengths (0.01, 0.1 and 1 M).

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