Journal of the Taiwan Institute of Chemical Engineers 000 (2015) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon

Chahrazed Djilani[a,*], Rachida Zaghdoudi[b,c], Fayçal Djazi[a,c], Bachir Bouchekima[d], Abdelaziz Lallam[e], Ali Modarressi[f], Marek Rogalski[f]

[a] Faculté de Technologie, Université du 20 Août1955, B.P 26 Skikda 21000, Algeria
[b] Faculté des sciences, Université du 20 Août1955, B.P 26 Skikda 21000, Algeria
[c] Laboratoire LRPCSI, Université du 20 Août1955, B.P 26 Skikda 21000, Algeria
[d] Laboratoire de Développement des Energies Renouvelables (LENREZA), Université Kasdi Merbah, BP 511 Ouargla 30000, Algeria
[e] Laboratoire de Physique et Mécanique Textiles de l'ENSISA (LPMT), Université de Haute Alsace, 11 rue Alfred Werner, F 68093 Mulhouse CEDEX, France
[f] Laboratoire de Chimie et de Méthodologies pour l'Environnement (LCME), Université Paul Verlaine, 1, Boulevard Arago 57078, France

ARTICLE INFO

Article history:
Received 21 March 2014
Revised 19 February 2015
Accepted 25 February 2015
Available online xxx

Keywords:
Apricot stones
Activated carbon
Dyes
Adsorption isotherm
Kinetic

ABSTRACT

The aim of this work is to study the properties of an activated carbon prepared from apricot stones by carbonisation for 1 h at 700 °C and chemical activation with a mixture of H_3PO_4 + HNO_3 and compared to a commercial activated carbon. The adsorbent materials were characterised with FTIR spectroscopy, XRD, SEM/EDX and surface chemistry. The maximum uptake of MB and MO onto the ASAC and CAC under optimised conditions was determined to be 99.5%. The absorption processes of MB and MO by ASAC and CAC were endothermic and exothermic, respectively. Acidic conditions promote the transfer of anionic dye (MO) molecules onto the ASAC and CAC surface by electrostatic attraction. The adsorbents were better able to remove the cationic dye than the anionic dye. The competitive adsorption of dyes favoured the MB on ASAC and CAC in the mixture solution. The Langmuir isotherm model and the pseudo-second order kinetic model were observed to fit the adsorption data well. The mechanism of the adsorption process was determined based on an intraparticle diffusion model. The results of this study will be useful for future scale-up using this apricot stone material as a low-cost adsorbent for the removal of cationic and anionic dyes.

1. Introduction

Dyes are primarily used in the textile industry, although substantial quantities are consumed for colouring various materials, such as leather, paper, plastics, petroleum products and food [1]. Dyes usually have a synthetic origin and complex chemical structure, which make them very stable to light and oxidation and very difficult to biodegrade [2,3]. The textile industry is one of the largest polluters in the world. Most dyes can cause damage not only to aquatic life but also to human beings because they are toxic, mutagenic or carcinogenic [4]. Therefore, the removal of dyes from waste effluent is of significant environmental importance [2,5]. Generally, the dyes that are used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulphur dyes [6,7]. Methyl orange, an anionic dye, belongs to the azo group of dyes, which consist of nitrogen-containing molecules. Methyl orange has been widely used in the textile, printing, paper, pharmaceutical and food industries. The presence of an azo group (N=N) on MO and its low biodegradability makes it a concern of environmental science [8]. Methylene blue (MB), a cationic dye, is commonly used as a temporary hair colourant and for colouring paper, dyeing cottons, wools, *etc.* It can cause eye burns and may be responsible for permanent injury to the eyes of humans and animals [9]. The removal of methyl orange (MO) and methylene blue (MB) from water is very important due to their toxicity. MO and MB were selected in this study as representative acidic (anionic) and basic (cationic) dyes, respectively, for the reasons stated above [3]. The removal of dyes from effluents in an economical manner is a major problem for the textile industry [10]. Various treatment processes, such as ozonisation, coagulation, ultrafiltration, oxidisation, photochemical degradation and adsorption, have been widely investigated for the removal of dyes from wastewater [1,4,11,12]. Among the numerous techniques designed for dye removal, adsorption is one of the most effective, and it has been successfully employed for the removal of dyes from wastewater [13]. Adsorption on activated carbon is commonly used due to its high efficiency, ability to separate a wide range of chemical compounds, simplicity of design and economic feasibility [14]. Activated carbons are widely used as adsorbents in wastewater treatment because of

* Corresponding author. Tel.: +213 791665403.
E-mail address: chahrazed_dj@yahoo.fr (C. Djilani).

http://dx.doi.org/10.1016/j.jtice.2015.02.025
1876-1070/

their high adsorption capacities, extremely high surface areas, micropore volumes, fast adsorption kinetics, relative ease of regeneration and amphoteric properties, which enable the adsorption of both cationic and anionic pollutants in effluent [15-17]. Nevertheless, commercially available activated carbons remain limited due to the high cost resulting from the use of non-renewable and expensive starting materials, such as coal [18]. However, researchers are attempting to produce cheaper, more effective and environmentally friendly activated carbons [19]. Recently, low-cost precursors have become the focus of researchers worldwide (for example, precursors from wastes and agricultural by-products, such as fruit stones [20], bagasse pith [21], coconut husks [22], rice husks [23], citrus fruit peels [24] and corncobs [25]).

The objectives of this work were to prepare activated carbon from apricot stones (kernels and shells) using carbonisation and chemical activation with a mixture of $H_3PO_4 + HNO_3$ as the activating chemicals; to use the activated carbon prepared from apricot stones (ASAC) as a nonconventional, natural, low-cost adsorbent for decolourising aqueous solutions of dye; and to compare the adsorption capacity of the prepared carbon material with that of commercial activated carbon (CAC) for the removal of dyes, namely methylene blue and methyl orange.

2. Materials and methods

2.1. Preparation of activated carbon (ASAC)

Local apricot stones, a by-product of food processing, were collected and washed in distilled water two times prior to separating the peels. The apricot stones (kernels and shells) were crushed and ground in a laboratory. The ground raw material was placed in ceramic crucibles and then introduced into an electric furnace. The carbonisation time was 1–2 h, and the treatment temperature ranged from 200 to 900 °C. The product obtained was washed with 10% hydrochloric acid to remove organic residues that had formed during the carbonisation process and then rinsed several times with distilled water while the pH was regularly checked. The carbonised materials were activated with $\{H_3PO_4 + HNO_3\}$ aqueous solutions, with the weight concentrations of both acids ranging from 10% to 90%. The mixture of the carbonised material and activating agent was stirred for 10 min at room temperature, boiled and stirred for 3 h. The solution was placed in an oven at 120 °C for 24 h. The solid obtained by filtration was washed several times with hot distilled water, then with cold water until neutral pH values were reached, indicating that the phosphates and nitrates were eliminated. Finally, the material was dried in an oven at a temperature of 110 °C for at least 12 h [26]. The particle size distribution of the activated carbon obtained in this manner was determined to be between 150 and 250 μm.

2.2. Characterisation of ASAC and CAC

The commercial (Riedel-De Haën; item No. 18001) and apricot-stone-based activated carbons were characterised by the methods described by Chahrazed et al. [26]. The surface acidity was estimated by mixing 0.2 g of ASAC and CAC with 25 ml of 0.05 N NaOH in a closed flask and agitating for 48 h at room temperature. The suspension was decanted, and the remaining NaOH was titrated with 0.05 N HCl. The surface basicity was measured by titration with 0.05 N NaOH after the incubation of 0.2 g of ASAC and CAC with 0.05 N HCl [27].

Surface area is the most important property of activated carbon adsorbents for its adsorption capacity. Generally, the higher the surface area, the larger is its adsorptive capacity [28]. Surface area of the adsorbent was determined by the method described by Shoemaker and Garland [29]. Then 0.5 g of adsorbent was placed in BOD bottles containing 50 mL of 0.015, 0.025, 0.05, 0.10 and 0.15 M acetic acid; a control was also prepared for each concentration without adsorbent. They were tightly closed and agitated for 1 h at 150 rpm. The samples were filtered using 0.45-μm filter paper. The filtrate was titrated with standard NaOH (0.1 mol/L) solution to find out the remaining concentration of acetic acid (C). The concentration of acetic acid remaining in each case (C) was divided by the number of moles of acetic acid (N) adsorbed per gram of the adsorbent to get the ratio, C/N. The slope of the linear plot of C/N vs. C yielded N_m value (*i.e.*, $N_m = 1/\text{slope}$). By substituting the N_m value in the following equation, surface area, A (m^2/g), was calculated:

$$A = N_m \times N_0 \times \sigma \times 10^{-20} \quad (1)$$

where N_0 is the Avogadro number, N_m the number of moles per gram required to form monolayer and σ is the molecular cross section area given in square Angstrom (21 Å) for acetic acid.

FTIR spectra of the activated carbons were obtained over the 4000–650 cm^{-1} range using a spectrophotometer (Spectrum One FTIR spectrometer). X-ray patterns were also determined for all samples. X-ray diffraction (XRD) studies were performed using a Bruker diffractometer, model D8 Advance, equipped with a Cu Kα source and a Lynxeyes fast detector (system θ–θ) operating at the monochromatic Kα_1 radiation wavelength of copper ($\lambda = 1.5406$ Å). The measured angular field ranged from $2\theta = 8$ to 100° for the ASAC and CAC. SEM-EDX studies of the carbonaceous materials were carried out on a HITACHI S-2360 N SEM, and elementary analysis was performed simultaneously using a JEOL JSM 840 microscope equipped with an EDX attachment. The materials were observed at different magnifications.

2.3. Batch equilibrium studies

The two different dyes used in this study were methylene blue (MB; molecular formula is $C_{16}H_{18}ClN_3S$; C.I. No. 52015; Mw = 319.85; Biochem Chemopharma) and methyl orange (MO; molecular formula is $C_{14}H_{14}N_3NaO_3S$; C.I. No. 13025; Mw = 327.33; Biochem Chemopharma). Dyes of commercial purity were used without further purification. The stock dye solutions were prepared by dissolving accurately weighed dyes in deionised water to a concentration of 1000 mg/L and subsequently diluted when necessary.

Adsorption studies of MO and MB were performed using ASAC and CAC as the adsorbents. The batch experiments were performed using a set of 250-ml stoppered flasks (Erlenmeyer flasks) containing a known quantity of adsorbent (0.010 g) and a pre-defined volume (100 ml in each flask) of dye solution at a fixed initial concentration (10 mg/L) with a constant solution pH. The flasks were then placed in a shaker at 200 rpm and a temperature of 25 °C. The samples were examined at specific time intervals, and the solutions were filtered at equilibrium using 0.45-μm filter paper to determine the equilibrium concentrations.

The initial and equilibrium concentrations were measured with a Shimadzu UV-1700 spectrophotometer at wavelengths of 665 and 465 nm for MB and MO, respectively.

The amount of adsorbate adsorbed at equilibrium, q_e (mg/g), was calculated using the following equation:

$$qe = \frac{(C_i - Ce) \times V}{W} \quad (2)$$

where W is the mass of adsorbent expressed in g, V is the volume of the solution in L and C_i and C_e are the initial and equilibrium concentrations, respectively, expressed in mg/L.

The effects of several operational parameters, such as the contact time, initial concentration (5–100 mg/L), agitation speed (50–300 rpm), pH of the solutions (3–10), dose of adsorbent (0.01–0.2 g) and temperature (20–40 °C), were investigated. The results were expressed as the removal efficiency (R %) of the adsorbent for MB and MO, which was defined as

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

Please cite this article as: C. Djilani et al., Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon, Journal of the Taiwan Institute of Chemical Engineers (2015), http://dx.doi.org/10.1016/j.jtice.2015.02.025