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The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon

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ABSTRACT

Jerusalem artichoke stalk based mesoporous activated carbon (MAC) has been studied for its potential adsorption removal of anionic (methyl orange, MO) and cationic dyes (methylene blue, MB). Batch adsorption experiments found that the adsorption data of both dyes were well fitted by Langmuir model and pseudo second-order kinetics. MB and MO adsorbed by MAC were of endothermic and exothermic nature, respectively. Acidic condition promotes the anionic dye molecules moving onto MAC surface by electrostatic attraction, while limits the initial adsorption rate of cationic dye. The intra-particle diffusion was involved in the whole diffusion process, but not the sole rate-controlling step. The calculated film diffusion coefficient (D_f) values, in the range of 10^{-6} to 10^{-8} cm^2/s, was two orders of magnitude higher than intra-particle diffusion coefficient (D_i) values, indicating the film diffusion controls the whole diffusion rates of the dye molecules moving from aqueous solution onto solid surface. Moreover, the D values for both dyes obtained in present study were superior to many reported carbon adsorbents. This higher D values were the result of more developed internal surface of MAC as higher mesoporosity, which promotes the diffusion rate.

Introduction

Wastewater containing azo-dyes was usually considered as one of the world widely serious environmental problems. Azo-dyes not only cause environmental esthetic problem, but also threaten human health [1,2]. Removing azo dye from wastewater is an urgent task for abbreviating the water pollution. Various techniques have been applied for the azo-dye removal, such as advanced oxidation technique, anaerobic degradation and physical adsorption. Advance oxidation was usually considered as a high efficiency technology, but it consumes a large amount of energy and chemical reagents which limits large-scale applications [3]. Biological process is time consuming and unstable because azo-dye molecular is oxygen-insensitive and the components of wastewater change in every batch effluents [4]. Physical adsorption is considered more effective and superior compared to the former techniques. The operation is simple and the treatment performance is not easily affected by toxic substances [5,6].

High efficiency adsorbents, such as agricultural solid wastes, natural clay materials and activated carbons prepared from cheap and renewable precursors have been attempted to remove dyes from aqueous solution [7–11]. However, the pore sizes of those adsorbents were mainly distributed in microporous ($d < 2$ nm) range, which were difficult for removal of the large azo-dye molecules [12]. Mesopore is the main transfer artery for large molecules, higher mesoporosity may benefit for the adsorbates transfer from liquid solutions to solid adsorbents [11]. Thus, developing activated carbon with high mesoporosity is supposed to be more effective for the adsorption of large molecules [8,11]. Recently, we have prepared a mesopore dominated activated carbon (MAC) from Jerusalem artichoke stalk (JAS). The maximum adsorption capacity of MAC to methylene blue (MB) was 374.5 mg/g [13]. The carbon exhibits a great potential for the azo-dyes removing from aqueous solution. However, the type of dyes, concentrations and environmental conditions changed in every bath effluent. The aims of this study were to explore the adsorption mechanism of anionic and cationic dyes by MAC under various environmental conditions. Methyl orange (MO) and MB will be used as model anionic and cationic dyes for evaluating the adsorption performance of MAC, respectively. Dyes adsorption using different factors, such as pH, initial dye concentration, adsorbent dosage and temperature on adsorption rates and

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Table 1
Component analyses of raw JAS, produced MAC and commercial carbons.

JAS			MAC	PAC	GAC
C (%)	46.04	Carbon yield (%)	36.15	–	–
H (%)	5.67	BET (m^2/g)	1632	1410	582
O (%)	47.87	Total volume (cm^3/g)	1.22	0.81	0.32
N (%)	0.42	Mesopore volume (cm^3/g)	1.10	0.59	0.10
VS (%)	95.73	Micropore volume (cm^3/g)	0.12	0.22	0.22
Ash (%)	5.05	Average pore width (nm)	3.0	2.3	2.2
Cellulose (%)	54.16	Point of zero charge	3.7	–	–
Semi-cellulose (%)	9.64				
Lignin (%)	8.67				

capacities were investigated as well. The result of this work may be helpful to assess the use of MAC in azo-dye wastewater treatment application.

Materials and methods

Materials and chemicals

MB and MO were used as model adsorbates, and were purchased from Sigma–Aldrich without further purification. The other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) without further purification. JAS was obtained from local farm, near Yantai city. The JAS was first washed thoroughly with distilled water to remove dust particles, and then dried at 105 °C. Table 1 lists the raw JAS contents in the proximate analysis. The preparation process was according to our previous study [13]: the samples were firstly soaked in $ZnCl_2$ solution with a $ZnCl_2$/JAS impregnation ratio of 2.68:1 (wt. %), then the mixture was put in a water bath at 80 °C for 8 h. After being dried, the impregnated samples were activated in a carbonization furnace at 528 °C for 60 min under nitrogen atmosphere. The activated products were cyclic washed with 3 M HCl and hot water until the washing solution was neutral, and then were dried.

Batch adsorption studies

Dye concentrations were determined at maximum absorbance (λ_{max}) of the two dyes (464 nm for MO, 664 nm for MB) by a UV–visible spectrophotometer (TU-1810, Purkinje Co. Ltd.). For initial pH value at acidic or basic condition, the dye samples were diluted by 0.1 M phosphate buffer solution before absorbance measurements. Batch adsorption experiments were performed in 50 ml conical flasks with 10 mg MAC and 25 ml of aqueous dye solutions. The mixture was shaken at a constant temperature using shaker incubator at 120 rpm at 30 °C for 4 h. All adsorption experiments were conducted in triplicate, and standard deviation was reported as error. Liquid samples were collected at predetermined time, centrifuged, and then analyzed the absorbance of supernatant at the λ_{max}. The amount of dye adsorbed onto MAC at time t (min), q_t (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where, C_0 is the initial dye concentration (mg/L), C_t is the supernatant concentration of dye at time t, V is the volume of solution (L) and m is the weight of MAC (g).

Analysis

The elemental analysis was conducted using an elemental analyzer (Vario MICRO cube, Elementar Co. Germany). Particle size of MAC powder was measured by Malvern Mastersizer 2000F particle size analyzer (Malvern Instruments Ltd., UK). The morphologies were conducted on a high-resolution scanning electron microscope (SEM, Hitachi S-4800, Japan). The pore properties analyzed by nitrogen adsorption at 77.15 K using an automatic pore size and surface area analyzer (Micromeritics, TriStar II 3020). The surface area was calculated using the BET equation, which is the most used model for determining the apparent surface area [14]. The total pore volume was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure of $P/P_0 = 0.99$. The mesoporous surface area and micropore volume were estimated using t-plot [14]. The surface organic functional groups of the samples were analyzed by Fourier transformed infrared spectroscopy (Nicolet 380 FT-IR). The zero charge point pH (pH_{PZC}) of MAC was determined by the final pH drift method [2].

Results and discussion

Characterization of MAC

The SEM images in Fig. 1 show the surface morphologies of raw JAS and produced MAC. Under magnification of 500× (Fig. 1a), the fiber buddle of raw JAS is compact, coarse and covered by deposited tarry substances. Numbers of stomas with an average diameter of 2 μm are orderly distributed on the surface under magnification of 2000× (Fig. 1b). Conversely, MAC displays irregular fragments instead of complete fiber bundle, as depicted in Fig. 1c. At a closer observation (magnification of 250,000× Fig. 1d), cavities were found to distribute around the surface. These cavities were resulted from the evaporation of impregnated $ZnCl_2$ derived compounds, leaving the space previously occupied by the reagent [11].

Fig. 2 shows the FTIR spectra of the chemical compositions of raw JAS and produced MAC. For the JAS, a wide band located at 3405.44 cm^{-1} and 2920.58 cm^{-1} represents O–H groups and C–H vibration [5,15]. The band at 1743.10 cm^{-1} is related to stretching of C=O groups. The band at 1635.48 cm^{-1} is due to the stretching of C=C vibrations in olefinic structures. The two bands at 1507.67 cm^{-1} and 1425.72 cm^{-1} may due to the C=C vibrations of aromatic ring. The stretching vibration of $-CH_3$ at 1374.15 cm^{-1} are related to methyl structures [10]. The peak at 1245.85 cm^{-1} indicates C–N stretching with amine or C–O vibration of carboxylic acid [16]. The adsorption peak at 1053.83 cm^{-1} and 616.62 cm^{-1} may responds to –C–C– and –CN stretching, respectively [15]. The spectra of activated carbon are different from those of raw materials. Many bands disappear, indicating the vaporization of organic matters. The carbon sample shows a wide band at 3420.22 cm^{-1}, which is due to the O–H vibrations of hydroxyl groups. The band located at 1621.56 cm^{-1} may be attributed to C=C vibrations. These results are agree with the report of Liou, where O–H and C=C vibrations of produced carbon by $ZnCl_2$ activation were found at 3425 cm^{-1} and 1604 cm^{-1}, respectively [10].

The nitrogen adsorption–desorption isotherms of resulting MAC at 77 K is depicted in Fig. 3a. It was found that the isotherm was more of type II character as defined by IUPAC classification [12]. This adsorption behavior exhibits a dominated mesoporous structure. The textural characteristics of produced MAC were summarized in Table 1. It can be seen that the BET surface area, total pore volume, mesopore volume and average pore width were greatly improved compared to the commercial carbons. Fig. 3b shows the pore size distribution of MAC calculated by the BJH method [14]. The pore size distribution curve suggests a highly mesoporosity owing to the narrow peak at 3.8 nm.

Adsorption isotherms

The adsorption isotherm describes the interact mechanism between adsorbate and adsorbent, and reveals the adsorption