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Adsorption properties of activated carbon from reed with a high adsorption capacity

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ABSTRACT

Activated carbon with a high adsorption capacity was prepared using reed from the Yellow River Delta of China as a low-cost raw material. The adsorption-desorption behavior of methylene blue (MB) onto the reed activated carbon (RAC) was studied in detail. The structure of RAC was characterized by scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy and nitrogen adsorption analysis. Based on a good fitting with the Langmuir isotherm model, and pseudo second-order kinetics, the adsorption behavior of MB on RAC can be considered mainly to be the monolayer adsorption process, and is related to the chemical functional groups on the surface of carbon. The maximum adsorption capacity of RAC obtained from the Langmuir isotherm equation at 30 °C is 704.23 mg/g. The high adsorption capacity can be attributed to its low polarity, numerous types of surface functional groups, high surface area and pore volume, and a hierarchal porous structure. The regenerating rate of the spent RAC saturated with MB was 85.15% after one regeneration cycle, indicating a good potential for commercial applications.

1. Introduction

Owing to extremely high surface areas, varied porous structures, large adsorption capacities, and fast adsorption kinetics, activated carbons can be used in a broad and growing range of environmental, health, safty and industrial applications, such as gas storage (Martin et al., 2013), recovery of ionic liquids (Lemus et al., 2012), catalyst supports (Yao et al., 2013), battery electrodes (Elazari et al., 2011), manufacture of electric double layer capacitors (Li et al., 2012), and purification and elimination of hazardous components in gas and liquid phases (Adinata et al., 2007; Salman and Hameed, 2012). Recently, due to ideal renewability and cost-efficiency, more agricultural biomass-based raw materials have been used to make high quality commercial activated carbons including coconut shell (Boopathy et al., 2013; Anirudhan and Sreekumari, 2011; Amuda et al., 2007), jackfruit peel (Foo and Hameed, 2012a,b; Prahas et al., 2008), pomegranate (punica granatum) pulp (Güzel et al., 2012), softstem bulrush (Xie et al., 2011), bagasse (Tseng and Tseng, 2006), rice husk (Chen et al., 2011), date stones (Belala et al., 2011), palm-trees (Chen et al., 2010), banana stalks (Salman and Hameed, 2012), reed (Chen et al., 2010), cattail (Shi et al., 2010), jute fiber (Senthilkumaar et al., 2010), hazelnut shell (Demirbasa et al., 2009; Imamoglu and Tekir, 2008), hevea brasiliensis seed coat (Hameed and Daud, 2008), bamboo (Hameed et al., 2007), durian shell (Chandra et al., 2007), and corncob (Tseng and Tseng, 2005). Most activated carbons derived from agricultural biomass-based raw materials exhibit the high surface areas and adsorption capacities. Foo et al. (Foo and Hameed, 2012a,b) prepared activated carbon from jackfruit peel via microwave-assisted NaOH activation, in which the specific surface area and the maximum adsorption capacity for methylene blue (MB) were 1286.7 m^2/g and 400.46 mg/g, respectively. Dural et al. (Dural et al., 2011) obtained activated carbon from posidonia oceanica dead leaves using $ZnCl_2$ as an activation agent, which specific surface area was 1483 m^2/g, and the maximum adsorption capacity for MB was 285.7 mg/g. However, due to lower adsorption capacities and surface areas of activated carbons derived from reed sources, the adsorption profiles of these materials have not been widely reported in the literature. Sharifirad et al. (Sharifirad et al., 2012) prepared phragmites australis (reed) derived carbons with a maximum adsorption capacity of 153 mg/g for MB using K_2CO_3 as an activating agent at

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800 °C. Fathy et al. (Fathy et al., 2012) obtained reed-derived carbon with a surface area of 318 m^2/g using H_3PO_4 activation at 450 °C.

Here, we used the renewable reed from Yellow River Delta of China as the raw materials to make a kind of reed activated carbon(RAC) with a hierarchal porous structure including microporous, mesoporous and macroporous structures, which was considered the main reason of the highly adsorption capacity. The detail structure of the reed activated carbon and the adsorption-desorption behavior for MB were also studied in detail. Adsorption method is an effective, simple, and economically feasible technique for the removal of organic dyes and pigments from wastewaters. It is necessary to studied the adsorption behavior of RAC in the solution,which can help us to understand the adsorption mechanism. The adsorption behavior of MB on RAC can be considered mainly to be a monolayer adsorption process, and is related to the chemical functional groups on the surface of carbon. The high adsorption capacity can be attributed to its low polarity, numerous types of surface functional groups, high surface area and pore volume, and a hierarchal porous structure. The regenerating rate of the spent RAC saturated with MB was 85.15% after one regeneration cycle, indicating a good potential for commercial applications.

2. Methods

2.1. Preparation of reed-derived carbon

2.1.1. Carbonization

Reed was collected from the Yellow River Delta in the Shandong province of China, and was cleaned and dried. The dried reed stalks (about 2 cm long) were charred in a furnace at 450 °C, with a ramp rate of 5 °C min^{-1} under an Ar flow. After the carbonization process and cooling, the produced reed char was ground into a powder in a mortar and screened using a 40-mesh sieve. Then, solid K_2CO_3 pellets were added as an activation agent, and mixed with the reed char in different mixture ratios (MRs: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0), defined as:

$$MR = \frac{W_{K_2CO_3}}{W_{char}} \quad (1)$$

where W_{K2CO3} and W_{char} are the dry weights of K_2CO_3 pellets (g) and reed char (g), respectively.

2.1.2. Activation

The char mixed with K_2CO_3 was put into the furnace under a flow of Ar gas, and heated with a ramp rate of 5 °C min^{-1} to maximum temperatures of 650 °C, 700 °C, 750 °C, 800 °C, 850 °C and 900 °C. After cooling to room temperature, the samples were washed with distilled water until they exhibited a neutral pH = 7. The washed wet products were then dried in an oven at 80 °C for 5 h, and weighed immediately after cooling to room temperature. The carbon yield is defined as the dry weight of activated carbon per weight of char utilized for activation.

2.2. Characterization

The morphologies and structure of RAC were observed using scanning electron microscopy (SEM) (JSM-6700F, Japan) and transmission electron microscopy (TEM) (JSM-2100, Japan). Fourier transform infrared spectrometer (FTIR) (TENSOR 27, Germany) was used to investigate the surface functional groups on RAC.

Textural characterization of all the samples was performed by nitrogen adsorption at −196 °C using a volumetric adsorption analyzer (V-sorb 2800 specific surface area and pore size analyzer). Prior to analysis, all samples were degassed for 4 h in vacuo at 300 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation; the micropore volume, micropore surface area, and external surface area were obtained using the t-plot method (Lippens and Deboer, 1965).

2.3. Adsorption

MB purchased from Sigma-Aldrich as a typical cationic dye is difficult to be degraded in natural environments (Foo and Hameed, 2012a,b; Berrios et al., 2012). Stock dye solutions were prepared by accurately dissolving 0.250 g of MB in 1 L distilled water. To prevent decolorization by direct sunlight, the stock solutions were stored in dark bottles and kept in a dark location before being used. Batch adsorption experiments were performed using 250 mL beakers containing 0.10 g adsorbent and 200 mL of the dye solution on a magnetic stirrer at 30 °C. In order to test the adsorption capacities of the RAC, different initial concentrations of MB solutions(100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L, and 500 mg/L, respectively) were selected as the start solution for the adsorption experiment. The dye concentration was analyzed every 5 min by using a double-beam UV–vis spectrophotometer (TU-1901 Double-beam ultraviolet-visible spectrophotometer) at 664 nm, until a constant concentration was obtained.

2.4. Regeneration

The regenerating feasibility of the spent RAC saturated with MB was evaluated using an ethanol desorption technique (Tanthapanichakoon et al., 2005). The typical desorption process is as follows: after the absorption process in 200 mL of 400 mg/L MB solution, the 0.1 g saturated RAC was separated and washed with distilled water. The wet RAC was added into another 250 mL beaker containing 80 mL of 95 vol.% ethanol, and stirred at 30 °C for 24 h. Then, the used RAC was separated, washed, and dried at 80 °C in an oven. In order to study the regeneration of RAC, the above dried RAC was used again in 200 mL of 400 mg/L MB solution using the same experimental conditions. The regeneration rate was defined as the ratio of MB uptake at equilibrium after and before regeneration.

3. Results and discussion

3.1. Effect of initial dye concentration

The effect of MR on the BET surface area and the carbon yield are shown in Fig. 1a. It is evident that the carbon yield decreased from 68.32% to 61.72% with increasing MR from 0.5 to 3. However, the BET surface area increased from 469.87 m^2/g to 1 000.46 m^2/g with MR increasing from 0.5 to 1, and then presented a steady decrease. The results show that the MR plays an important role for the carbon yield and porous structure. Actually, the enlargement of the porous structure of RAC are mainly associated with the oxidation-reduction reaction of chemical agents with reed char (Eqs. (2) and (3)), which can separate and degrade reed char and help to form micropores and mesopores.

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad (2)$$

$$2K_2O + C \rightarrow 4K + CO_2 \quad (3)$$

Additionally, the produced metals and alkaline or carbonate compounds can be intercalated into the carbon matrix, assisting in the formation of porous structures in the reed char. Simultaneously, the evolution of CO_2 might also be responsible for expansion of reed carbon and physical activation of the carbon surface. Therefore, the MR plays a key role in pore development in the activation process of reed char. However, excess K_2CO_3 can also promote a vigorous redox reaction and gasification, which would destroy the carbon framework and lead to a dramatic decrease in the accessi-