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Insights into properties of activated carbons prepared from different raw precursors by pyrophosphoric acid activation

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ABSTRACT

Low-cost activated carbons (ACs) were prepared from four kinds of solid wastes: petroleum coke, *Enteromorpha prolifera*, lignin from papermaking black liquid and hair, by pyrophosphoric acid ($H_4P_2O_7$) activation. Thermo-gravimetric analysis of the pyrolysis of $H_4P_2O_7$-precursor mixtures implied that $H_4P_2O_7$ had different influences on the pyrolysis behavior of the four raw materials. N_2 adsorption/desorption isotherms, scanning electron microscopy, Fourier transform infrared spectroscopy and adsorption capacities for dyes were used to characterize the prepared activated carbons. AC derived from *E. prolifera* exhibited the highest surface area (1094 m^2/g) and maximum monolayer adsorption capacity for malachite green (1250 mg/g). Kinetic studies showed that the experimental data were in agreement with the pseudo-second-order model. The adsorption isotherms were well described by the Langmuir isotherm model, indicating the adsorption of dye onto the ACs proceeded by monolayers.

Introduction

Activated carbons (ACs) have been extensively developed as effective adsorbents for the removal of inorganic/organic pollutants. The adsorption characteristics of ACs rely on their surface area, porous structure and surface chemical groups. The starting materials, activating agents and activation methods have significant influence on these properties. Generally, KOH, NaOH, $ZnCl_2$ and H_3PO_4 have been widely used as chemical activating agents for the preparation of ACs (Miao et al., 2013; Njoku et al., 2014; Rambabu et al., 2013; Wang et al., 2014). Pyrophosphoric acid, $H_4P_2O_7$, can be obtained by the dehydration of phosphoric acid at 213°C. In recent years, some researchers have applied $H_4P_2O_7$ as a novel activating agent to prepare ACs (Cheng et al., 2014; Kong et al., 2013; Liu et al., 2012). They found that $H_4P_2O_7$ has stronger dehydrating ability than H_3PO_4, which could create pores at low temperature. In addition, the ACs produced by $H_4P_2O_7$ activation exhibited several excellent properties, such as high surface area, high mesopore content, and abundant acidic functional groups, which endowed them with good sorption affinities and capacities. However, previous works only focused on the preparation of ACs from lignin or leather by pyrophosphoric acid activation. There are no reports comparing the characteristics and adsorption properties of activated carbons prepared from different raw materials using pyrophosphoric acid as activating agent. Hence, it was necessary to carry out this research.

In fact, a large variety of precursors have been used for producing ACs including Bois carré seeds (Largitte and Lodewyckx, 2014), African biomass residues (Gueye et al., 2014), olive fruit stones (Obregón-Valencia and Sun-Kou, 2014), lotus stalk (Liu et al., 2012), seaweeds (Wang et al., 2014), and mushroom root (Cheng et al., 2014). Petroleum coke (PK), a by-product of the petroleum industry, is a common raw

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material for AC preparation due to its high carbon content and low ash content (Jiang et al., 2008; Rambabu et al., 2013; Wu et al., 2005). Lignin from papermaking black liquid (LG) is widely utilized to prepare high value-added products, for example activated carbon. *Enteromorpha prolifera* (EP) is a marine biomass waste and is widely available, especially in the Asia-Pacific region (Özer et al., 2005; Wang et al., 2014). Hair (HR) has also been proved to be a good candidate for the synthesis of porous carbon (Guo et al., 2013). These materials possess typical coke-based, lignocellulosic, algous and fibrous properties. Thus, this study investigated the different roles of pyrophosphoric acid in reacting with these starting materials.

Synthetic dyes are extensively applied in many industries, *e.g.*, paper, textile, leather tanning, printing, rubber and cosmetics (Bensalah et al., 2009; Yagub et al., 2014). Based on up-to-date data, the worldwide production of dyes is over 7×10^5 ton annually, and approximately 15% of dye-containing wastewater is discharged into the environment (Foo and Hameed, 2010b; Sen et al., 2010). Furthermore, dye wastewater has currently become one of the world's serious environmental problems due to the dyes' highly carcinogenic nature, mutagenic toxicity and physicochemical stability (Mahmoodi et al., 2011). Therefore, various methods, such as coagulation, photodegradation, membrane separation, microbial degradation, chemical oxidation and adsorption have been developed for the removal of dye from wastewater (de Luna et al., 2013; Toor and Jin, 2012; Vučurović et al., 2014; Xue et al., 2014). Among these technologies, adsorption is considered to be one of the most effective methods due to its simple design and ease of operation. Currently, ACs are widely used as adsorbents for dye removal from wastewater in commercial systems because of their large surface area, good thermo-stability, high mechanical strength, polymodal porous structure, variable surface chemical composition, high adsorption capacity and low cost.

In this study, pyrophosphoric acid was employed as activating agent for the preparation of ACs. The resultant carbons were characterized by scanning electron microscopy (SEM), pore structure analysis and Fourier transform infrared spectroscopy (FTIR). The adsorption capacity of the ACs was evaluated using Acid Brilliant Scarlet (anionic dye) and Malachite Green (basic dye) as the model adsorbates. The effects of adsorbent type and contact time were investigated to provide information on the adsorption characteristics of dyes on the four ACs. In addition, adsorption kinetics and isotherm tests were also performed to determine the adsorption rates and maximum adsorption capacities of the four ACs, as well as to analyze the adsorption mechanisms.

1. Experimental

1.1. Chemicals and materials

Pyrophosphoric acid (45 wt.%), analytical grade Acid Brilliant Scarlet (GR) and Malachite Green (MG) were purchased from a chemical company (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). All stock solutions were prepared by dissolving accurate amount of the dyes in distilled water. Various concentrations of dye solutions were diluted with distilled water. The molecular formulas of GR and MG are $C_{22}H_{14}N_4Na_2O_7S_2$ and $C_{23}H_{25}ClN_2$, and the molecular weights are 556.49 and 364.92, respectively. All waste materials were collected and cut into pieces with diameter of 0.425 mm for further use.

1.2. Preparation of the absorbents

The four raw materials (PK, EP, LG and HR) were impregnated with $H_4P_2O_7$ at a ratio of 1.5:1 (W/W) for 12 hr. Activation was achieved by heating the mixture in an electric resistance furnace (KSY-4D-16, Longkou Furnace Factory, Longkou, China) to the temperature of 450°C. The heating rate was 10°C/min and the preservation time was 60 min. The obtained samples were washed with distilled water until the pH of 6–7 was achieved. Then the samples were dried, ground, and sieved to the particle size range of 0.150–0.075 mm. The activated carbons (ACs) prepared by PK, EP, LG and HR were denoted as PCAC, EPAC, LGAC and HRAC, respectively.

1.3. Characterization

To measure how pyrophosphoric acid affected the thermal stability of the different raw materials, the thermal decomposition of the mixtures was analyzed using thermo-gravimetric analysis (SDT Q600, TA Instruments Co., Ltd, New Castle DE, USA). The surface morphologies of ACs were evaluated by employing a scanning electron microscope (S-520, Hitachi Ltd., Tokyo, Japan). The porous structure parameters of ACs were determined through N_2 sorption/desorption isotherms by using a surface area analyzer (JWBK122W, Beijing JWGB Sci. & Tech. Co., Ltd, Beijing, China). The surface functional groups of ACs were qualitatively characterized by using a Fourier transform infrared spectroscopy (Avatar 370, Thermo Nicolet Corporation, New York, USA).

1.4. Batch adsorption experiments

The adsorption experiments were conducted to assess the adsorption capacities of the four carbons. Each carbon (0.025 g) was mixed with 50 mL of dye solution in 250 mL Erlenmeyer flasks. The flasks were agitated at 170 r/min using a thermostatic water bath oscillator at room temperature. In kinetic tests, the initial concentrations of the dyes were 100 mg/L. The samples were withdrawn at predetermined intervals to investigate the effect of contact time. The samples were separated from the carbon particles by filtration. The residual concentrations of GR and MG were determined by using a UV–vis spectrophotometer (722E, Shanghai Spectrum Instruments Co., Ltd, Shanghai, China) at the maximum absorption wavelengths of 511 and 618 nm, respectively. In the adsorption isotherm tests, the initial concentrations of GR ranged from 50 to 600 mg/L and the initial concentrations of MG ranged from 100 to 600 mg/L. Blank control experiments were designed and conducted as described above. The amount of dye adsorbed, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of dye, V (L) is the volume of dye solution and W (g) is the mass of adsorbent.