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Preparation of activated carbon from Iris tectorum with different ammonium phosphates activation and removal of nickel from aqueous solution

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ABSTRACT

The preparation of activated carbons (AC-$(NH_4)_xH_yPO_4$) from Iris tectorum (IT) with three kinds of ammonium phosphates ($(NH_4)_2HPO_4$, $NH_4H_2PO_4$ and $(NH_4)_3PO_4$) activation was investigated, with a special attention paid to the effect of these $(NH_4)_xH_yPO_4$ on both physical and chemical properties. The prepared carbons were characterized by scanning electron microscope (SEM), N_2 adsorption/desorption isotherms, Fourier transform infrared spectroscopy (FTIR), and Boehm's titration. The surface area and total pore volume of AC-$(NH_4)_3PO_4$ were much higher than AC-$(NH_4)_2HPO_4$ and AC-$NH_4H_2PO_4$, while AC-$(NH_4)_2HPO_4$ had largest micropore volume ratio. Boehm's titration results suggested that AC-$(NH_4)_2HPO_4$ possessed more acidic functional groups than AC-$NH_4H_2PO_4$ and AC-$(NH_4)_3PO_4$. Batch adsorption studies were carried out to compare adsorptive performances of the carbons toward Ni(II). The adsorption equilibrium data were in good agreement with Langmuir model. The maximum Ni(II) adsorption capacities of AC-$(NH_4)_2HPO_4$ (40.00 mg/g) was higher than that of AC-$NH_4H_2PO_4$ (38.61 mg/g) and AC-$(NH_4)_3PO_4$ (34.60 mg/g), resulting from the carbons higher content oxygen-containing functional groups which could adsorb more Ni(II) by cation exchange and electrostatic attraction.

1. Introduction

The existence of heavy metals in the aquatic environment has become a matter of great concern to human since they cannot be destroyed or degraded, and pollution regarding heavy metals represents a compelling problem due to their toxicity and accumulation effect through the food chain, which will result in serious ecological and health problems [1]. Nickel (Ni) is considered to be one of the most common heavy metal contaminants and its compounds pose serious threat to human [2]. A large number of techniques, such as coagulation, precipitation, ion exchange, membrane filtration and adsorption on eliminating Ni(II) in the wastewater are designed for this reason [3–6]. Since activated carbon has extended surface area, highly porous structure and special surface reactivity [7], adsorption onto activated carbon proves to be an effective method for treating Ni(II) contaminated wastewater [8].

Generally, the preparation of activated carbon is usually divided into physical activation and chemical activation. In chemical activation, the activating agents mainly used are H_3PO_4, $ZnCl_2$ and KOH. Preparing activated carbons with well-developed porosity and excellent adsorption capacity using H_3PO_4, $ZnCl_2$ and KOH as activating agents have been widely investigated by many researchers [9–13]. However, using $ZnCl_2$ as the activating agent will have harmful effects on the environment and KOH could corrode the instruments. Therefore, seeking alternative chemicals which can be used as activating agents has become the focus of our attention. Benaddi et al. [14] have reported the preparation of activated carbons with various pore distribution and surface properties using diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as activating agent. $(NH_4)_2HPO_4$ can be obtained from the decomposition of ammonium phosphate ($(NH_4)_3PO_4$) and can transform into ammonium dihydrogen phosphate ($NH_4H_2PO_4$) at the temperature higher than 155 °C [14]. The effect of transformation of $(NH_4)_xH_yPO_4$ during the activation process on the final carbons still needs further investigation. Accordingly, in order to further investigate the mechanisms of $(NH_4)_xH_yPO_4$ affecting the porous characteristics and surface chemical properties of the final carbons, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ and $(NH_4)_3PO_4$ were chosen as the activating agents to prepare activated carbons using Iris tectorum (IT) as the precursor. To our knowledge, there is little information about the feasibility of preparing activated carbon with ammonium phosphates activation.

IT is a kind of herbaceous plant, which has high medical values and anti-inflammatory effect. In previous work of our team, we used IT as precursor to prepare activated carbon with high surface,

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well-developed porous structure and excellent adsorption capacity [15]. In this study, three kinds of ammonium phosphates ($(NH_4)_xH_yPO_4$), *i.e.* $(NH_4)_2HPO_4$, $(NH_4)_2HPO_4$ and $(NH_4)_3PO_4$ were used to activate IT. The main purposes of this study are (1) to investigate the effect of $(NH_4)_xH_yPO_4$ species on the final carbons; (2) to comprehensively evaluate the physical and chemical properties of the carbons, such as specific surface area, pore size distribution, pore volume and surface oxygen-containing functional groups; (3) to investigate the adsorption performances of the carbons toward Ni(II).

2. Materials and methods

2.1. Materials

Iris tectorum (IT) used as the raw material was obtained from Liaocheng of Shandong province in China. The sample was dried at 60 °C for 72 h and then crushed and sieved to particles of a desired size fraction of 0.1–0.2 mm for experimental use. Nickel chloride (MW = 237.69, chemical formula $NiCl_2{\bullet}6H_2O$) was chosen as the adsorbate. Diammonium hydrogen phosphate (MW = 132.06, chemical formula $(NH_4)_2HPO_4$)), ammonium dihydrogen phosphate (MW = 115.02, chemical formula $NH_4H_2PO_4$), ammonium phosphate (MW = 203.13, chemical formula $(NH_4)_3PO_4{\bullet}3H_2O$) were used as activating agents. All chemical reagents used in this study were of analytical grade.

2.2. Preparation of activated carbons with $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$ and $(NH_4)_3PO_4$ activation

Ten grams of IT was impregnated with 37.5 g of 40 wt.% concentration $(NH_4)_2HPO_4$ at a ratio of 1:1.5 (g IT:g $(NH_4)_2HPO_4$) for 10 h with occasional stirring. In order to compare the differences of the prepared carbons with the activated carbons activated with $(NH_4)_2HPO_4$ in the aspects of physical and chemical characteristics, the impregnation ratio of the other two activating agents ($NH_4H_2PO_4$ and $(NH_4)_3PO_4$) was also maintained at 1:1.5 (g IT:g $(NH_4)_xH_yPO_4$).Then the samples were transferred to microwave oven (MKX-M1-Q, Qingdao) with radiation power 700 W and radiation time 20 min. The varied parameters were investigated (radiation power from 500 to 800 W and radiation time 10–25 min) to determine the optimal preparation conditions. After cooling to room temperature naturally, the obtained samples were washed with deionized water repeatedly until pH of the washed solution became steady. The carbons were then dried at 105 °C for 10 h. Finally, the samples were crushed to particle size of 104–150 μm. The carbons activated with $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ and $(NH_4)_3PO_4$ were referred to as AC-$(NH_4)_xH_yPO_4$:AC-$(NH_4)_2HPO_4$, AC-$NH_4H_2PO_4$, AC-$(NH_4)_3PO_4$, respectively.

2.3. Characterization of IT-$(NH_4)_xH_yPO_4$ and AC-$(NH_4)_xH_yPO_4$

The specific surface areas and porous properties of the carbons were determined by N_2 adsorption/desorption isotherms measured at 77 K with a surface area analyzer (Quantachrome Corporation, USA). The surface micrographs of the samples were observed through scanning electron microscope (JEOL JSM-7600F SEM, Japan). Boehm's titration method [16] was employed to quantify the acid surface oxygen-containing functional groups of the carbons. The pH at the point of zero charge (pH_{pzc}) was determined from a batch equilibrium method [17]. The FTIR spectra of the carbons were performed using a Fourier transform infrared spectrometer (Fourier-380FTIR, USA) to detect surface oxygen-containing functional groups in the wavelength range 400–4000 cm^{-1}.

2.4. Adsorption studies

Ni(II) and the three carbons were designated as the adsorbate and the adsorbents in batch adsorption experiments. In pH experiments, the initial pH was adjusted with 0.1 M HCl and 0.1 M NaOH and measured using a pH meter (Model pH S-3C, Shanghai, China). NaCl and $CaCl_2$ were chosen to evaluate the separate effect on Ni(II) onto the carbons. In adsorption isotherm experiments, 0.035 g of adsorbent was introduced into a series of 150 mL conical flasks which contain 50 mL solution with a specific amount of Ni(II) (20–55 mg/L), the flasks were then transferred to a thermostatic oscillator (SHA-B, Shanghai, China) and shaken at a pre-set temperature (20, 30, 40 °C) for 48 h at a speed of 125 rpm. Our preliminary experiments demonstrated that 48 h was enough for adsorption equilibrium. The blank experiments were also carried out to determine the possible solute loss on the walls of flasks. The concentrations of Ni(II) before and after adsorption were determined using a UV–vis spectrophotometer (UV-754, Shanghai) at the maximum wavelength of 530 nm.

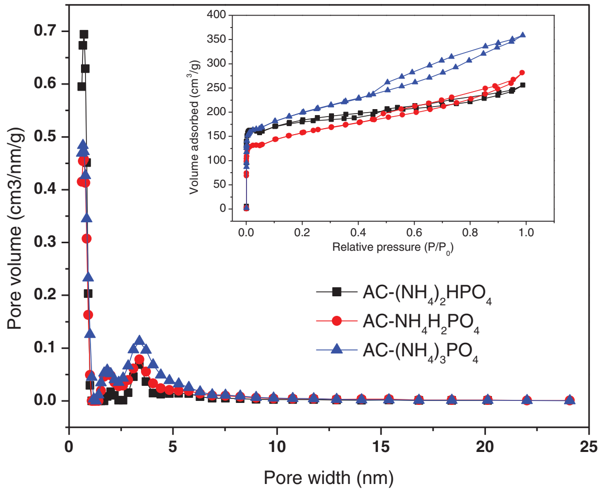

Fig. 1. Pore size distribution and N_2 adsorption/desorption isotherm (inset) of AC-$(NH_4)_2HPO_4$, AC-$NH_4H_2PO_4$, AC-$(NH_4)_3PO_4$.

The Ni adsorption capacity at equilibrium (Q_e, mg/g) was calculated according to the following equation:

$$Q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/L) represent the initial and equilibrium concentration of Ni(II). V (L) is the solution volume and W (g) represents the weight of adsorbent sample used.

3. Results and discussion

3.1. Characterizations of IT-$(NH_4)_xH_yPO_4$ and AC-$(NH_4)_xH_yPO_4$

3.1.1. Textural characteristics and surface morphology of IT-untreated and AC-$(NH_4)_xH_yPO_4$

The N_2 adsorption/desorption isotherm tests are performed to determine the textural parameters of the carbons, such as specific surface area (S_{BET}), total pore volume (V_{tot}), micropore volume, mean pore diameter (D_p). Fig. 1 shows the pore size distribution and N_2 adsorption/desorption isotherms of the three carbons. The textural parameters were calculated and summarized in Table 1. From Fig. 1, it can be seen that the carbons have large differences in specific surface area and pore volume. The majority of the pores fall into the range of mesopores and micropores (<8 nm), especially micropores. As shown in Table 1, AC-$(NH_4)_3PO_4$ gave the highest specific surface area and pore volume, whereas AC-$(NH_4)_2HPO_4$ had the highest micropore volume and micropore volume ratio. AC-$NH_4H_2PO_4$ only had lower specific surface area. Different molecular sizes of these $(NH_4)_xH_yPO_4$ caused different micropore sizes distribution in the carbons [18]. $(NH_4)_3PO_4$ can convert to lower-sized $NH_4H_2PO_4$. Accordingly, AC-$(NH_4)_3PO_4$ had the highest pore volume.

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