



Amination of activated carbon for enhancing phenol adsorption: Effect of nitrogen-containing functional groups

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ABSTRACT

To study the contribution of different nitrogen-containing functional groups to enhancement of phenol adsorption, the aminated activated carbons (AC) were characterized by N₂ adsorption/desorption, XPS, Boehm titration, and pH drift method and tested for adsorption behaviors of phenol. Adsorption isotherm fitting revealed that the Langmuir model was preferred for the aminated ACs. The adsorption capacity per unit surface area (q_m/SSA_{BET}) was linearly correlated with the amount of pyridinic and pyrrolic N, which suggested that these two functional groups played a critical role in phenol adsorption. The enhancement of adsorption capacity was attributed to the strengthened π - π dispersion between phenol and basal plane of AC by pyridinic, pyrrolic N. The adsorption kinetics was found to follow the pseudo-second-order kinetic model, and intraparticle diffusion was one of the rate-controlling steps in the adsorption process.

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1. Introduction

Phenolic wastewater, generated from chemicals, pharmaceuticals, petroleum, coal gasification, papermaking, wood, rubber, dye, and pesticide industries, is highly toxic and harmful [1]. Phenols in such wastewaters are the priority pollutants by the US EPA and China since they are not only carcinogenic but also cause unpleasant taste and odor even at low concentrations [2,3]. In China, according to the Chinese integrated wastewater discharge standard (GB 8978-1996), the maximum permitted concentration of volatile phenols is 0.5 mg/L for standard A effluent and 2.0 mg/L for standard C effluent [4]. Consequently, various technologies have been developed to treat phenolic wastewater. Among them, adsorption is an effective technology for removal of phenols from wastewater or other aqueous solutions [5].

Activated carbon (AC) is an excellent adsorbent due to its high surface area, well-developed internal pore structure, and tunable surface chemistry [6,7]. Besides the physical or porous structure [8], the surface chemistry of AC is considered as the main factor in the adsorption mechanism from phenol aqueous solutions [9]. Oxidation, a common modification method, introduces oxygen atoms

into the carbon matrix to modify the surface chemistry of AC [10]. However, a consistent conclusion has been drawn that AC treated by oxidation shows a significantly acidic character and a low phenol adsorption capacity [11]. The decrease in adsorption capacity can be ascribed to the increase of the oxygen-containing functional groups that attract and localize the π -electrons of basal plane on the carbon surface to reduce the interaction between phenolic ring and basal plane [12]. Moreover, these acidic groups, particularly carboxylic groups, create water clusters through H-bonding, thus reducing the accessibility and affinity of the phenol molecules to the inner pore structure [13].

However, the enhanced adsorption of phenols is observed for the AC modified by nitrogenation, another widely used method for modification of surface chemistry of carbon materials. Nitrogenation introduces nitrogen-containing functional groups onto the carbon surface, such as $-NH_2$, pyridinic, pyrrolic, and quaternary nitrogen groups [14], and the resulting carbon is basic in character. The AC modified with ammonia aqueous solution at room temperature shows a higher adsorption capacity toward 2,4-dichlorophenol [15]. The AC treated by urea at 450 °C exhibits a nearly 50% increase in phenol adsorption [16]. Similarly, the AC modified with ammonia gas at high temperature shows more than 20% improvement in adsorption capacity for phenol [17]. The enhancement of phenols adsorption is associated with the nitrogen-containing functional groups introduced into the carbon surface. It is speculated that pyridinic groups possibly relates to slight increase of phenol adsorption on the nitrogen-rich microporous AC compared with nitrogen-poor

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AC prepared from a mixture of polymer and coal-tar pitch [18]. However, the evidence is still weak and the contribution of different nitrogen-containing groups to the adsorption capacity of AC is not very clear. Therefore, further investigation into the effect of amination on the adsorption behavior is necessary.

In the present work, nitrogen-containing functional groups were introduced to the AC structure by thermal treatment under ammonia atmosphere. The isotherm data for adsorption of phenol were fitted with the Langmuir and Freundlich models. The parameter q_m/SSA_{BET} was created to discuss the correlation between adsorption capacity and nitrogen-containing groups.

2. Material and methods

2.1. Preparation of aminated ACs

A wood-based AC (Xinsen Carbon Industry Co. Ltd., China) was crushed, sieved to 15–40 mesh, and then treated with 1 M HCl solution for six hours to remove metal ions. The acid-treated AC was washed with deionized water until circum-neutral pH of the supernatant and dried at 105 °C for 24 h prior to use. This acid-treated AC was denoted as ACA. The aminated ACs were prepared by thermal treatment of ACA at 250, 450, 650, and 850 °C for 2 h in a tube furnace. A mixed gas (ammonia and nitrogen) flowed through the quartz tube from start to end of aminated treatment. The flow rates of ammonia and nitrogen were 20 and 60 mL/min (room temperature), respectively. ACN250 represented ammonia treatment of ACA at 250 °C.

2.2. Porosity of AC

The porous properties of the AC samples were determined by N₂ adsorption/desorption in a Builder SSA-4200 instrument. The AC samples were separately degassed at 300 °C for 2.5 h in a vacuum environment before measurement. The specific surface area was determined by the BET equation, and the total pore volume was calculated from the near saturation uptake ($P/P_0 = 0.99$). The mesopore volume, mesopore surface area, and pore size distribution were calculated by the BJH method.

2.3. Surface chemistry of AC

Boehm titration was conducted to determine the number and type of surface oxygen groups [19]. 0.5 g of sample was placed into 25 mL of the solution (0.05 M of NaOH, Na₂CO₃, or NaHCO₃) for 24 h to reach equilibrium. The acidic oxygen-containing surface groups were determined by back titration with 0.05 M HCl solution. The total content of basic groups was measured with 0.05 M HCl solution. pH_{pzc} was the pH value when the charge on the AC surface was zero. The pH_{pzc} was determined by the pH drift method. 50 mL of a 0.01 M KNO₃ solution was adjusted to successive initial values (pH_{initial}) between 2 and 12, by adding either HNO₃ or KOH. Then 0.15 g AC was added to the KNO₃ solution with a constant stirring at room temperature. The final pH, reached after about 48 h, was noted as pH_{final}. The pH_{pzc} is the point when pH_{initial} was equal to pH_{final}.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos XSAM800 equipped with Al K α X-ray source (1486.6 eV, anode operating at 12 kV, and 15 mA). The binding energies were calibrated based on the graphite C1s peak at 284.5 eV. The spectra was fitted with a Gaussian (80%)–Lorentzian (20%) mixed function after subtraction of a Shirley background using XPS Peak 4.1 software.

2.4. Adsorption of phenol

Batch adsorption experiments were conducted at 30–50 °C by agitating 0.1 g AC with 100 mL phenol solution of desired concentration (100–1000 mg/L) in a stoppered conical flask in a thermostat shaker at 150 rpm for 24 h. When reaching equilibrium, the phenol solution was separated from the adsorbent. The final concentration of phenol was analyzed using an ultraviolet spectrophotometer at a wavelength of 269 nm. The amount of uptake capacity at equilibrium, q_e (mg/g), was calculated by Eq. (1)

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

where q_e (mg/g) is the amount adsorbed onto the AC at equilibrium, C_0 and C_e (mg/L) are the initial and equilibrium concentrations of the solution, respectively, V (L) is the volume of the solution, and m (g) is the mass of AC.

The effect of solution initial pH on phenol adsorption was studied over a pH range of 2–12 at 30 °C. The pH was adjusted using 0.1 M HCl or 0.1 M NaOH. The phenol concentration was fixed at 1000 mg/L, with AC dosage of 0.1 g/100 mL.

The kinetics studies were performed at 30 °C, and solution pH was not adjusted. The initial concentration was set at 1000 mg/L, and the samples were separated at predetermined time intervals.

3. Results and discussion

3.1. Characterization of AC

The results of porosity characterization are presented in Table 1. The wood-based AC (ACA) was a highly mesoporous carbon with large specific surface area (SSA_{BET} , 1618 m²/g), pore volume (V_t , 1.06 cm³/g) and high percentage of a mesoporous structure (35% for SSA_{meso} and 65% for V_{meso}). The higher the aminated temperature was, the lower the SSA_{BET} and pore volume were. At an amination temperature of 650 °C, the SSA_{BET} and V_t of AC displayed slight reduction; and SSA_{meso} and V_{meso} decreased to 507 m²/g and 0.52 cm³/g, respectively. When amination temperature reached 850 °C, an obvious decrease in surface area and pore volume was observed.

The results obtained from Boehm titration together with pH_{pzc} are presented in Table 2. The amount of total acid of the aminated AC decreased with increasing amination temperature, and the concentration of carboxyl decreased from 0.349 to 0.082 meq/g. By contrast, a noticeable increase was observed in the concentration of total base with amination temperature increasing. The basic ACs were obtained by amination of the acid parent AC. This was confirmed by the pH_{pzc} that increased from 5.80 for the parent AC to 9.78 for ACN850. The enhancement of alkalinity was attributed to the decrease of oxygen-containing acid groups and the formation of nitrogen-containing basic groups via oxygen-containing groups reacting with ammonia.

The deconvoluted XP N1s spectra of the parent and aminated ACs are shown in Fig. 1, and the elemental composition is listed in Table 3. According to the spectra and references [20,21], the N1s was deconvoluted into five different types of N-containing species: N1 (pyridine, ~398.7 eV), N2 (imine/amide/amine, ~399.5 eV), N3 (pyrrolic, ~400.1 eV), N4 (quaternary N, ~401.3 eV), and N5 (N-oxide, ~403.1 eV). The surface nitrogen content of the aminated ACs increased with amination temperature. The highest content of total nitrogen (2.80%) was observed in ACN850. This showed that high amination temperature was favorable to the formation of nitrogen-containing functional groups on the AC surface. However, the concentration variation of specific nitrogen-containing groups was different from that of total nitrogen. When amination temperature exceeded 450 °C, more N1 and N3 species formed on

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