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Behavior of phenol adsorption on thermal modified activated carbon[☆]Dengfeng Zhang^{*}, Peili Huo, Wei Liu

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ABSTRACT

Adsorption process is acknowledged as an effective option for phenolic wastewater treatment. In this work, the activated carbon (AC) samples after thermal modification were prepared by using muffle furnace. The phenol adsorption kinetics and equilibrium measurements were carried out under static conditions at temperature ranging from 25 to 55 °C. The test results show that the thermal modification can enhance phenol adsorption on AC samples. The porous structure and surface chemistry analyses indicate that the decay in pore morphology and decrease of total oxygen-containing functional groups are found for the thermal modified AC samples. Thus, it can be further inferred that the decrease of total oxygen-containing functional groups on the modified AC samples is the main reason for the enhanced phenol adsorption capacity. For both the raw sample and the optimum modified AC sample at 900 °C, the pseudo-second order kinetics and Langmuir models are found to fit the experimental data very well. The maximum phenol adsorption capacity of the optimum modified AC sample can reach 144.93 mg·g⁻¹ which is higher than that of the raw sample, i.e. 119.53 mg·g⁻¹. Adsorption thermodynamics analysis confirms that the phenol adsorption on the optimum modified AC sample is an exothermic process and mainly *via* physical adsorption.

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1. Introduction

The phenolic compounds are highly carcinogenic and toxic even at low concentration [1]. Thus, the removal of phenol from wastewater is extremely necessary. Hitherto, various treatment technologies including adsorption [2], biodegradation [3], oxidation [4], precipitation [5], ion exchange [6] and solvent extraction [7] have been developed for the removal of phenol from wastewater. It is widely accepted that activated carbon (AC) is the most frequently-used adsorbent since it has well-developed porous structure and special surface chemistry property [8]. Therefore, AC has been widely used in environmental monitoring [9], environmental protection [10], catalyst support and electrode material preparation [11,12]. For phenolic compound adsorption, usage of AC is also considered as a prevalent method [13–15].

Research has shown that the properties of the adsorbent, adsorbate and the operational parameters will influence the liquid-phase adsorption process [16]. Among them, the porous structure and surface chemistry property of the adsorbent act dominant roles in the adsorption process [17]. Thus, for the adsorption system formed by phenol and AC, most investigations were carried out to modify the porous structure and surface chemistry of AC in order to enhance phenol adsorption [2,

18–20]. Hitherto, it has been found that usage of chemical agents, such as potassium hydroxide (KOH) [2], zinc chloride (ZnCl₂) [18], potassium carbonate (K₂CO₃) [19], and phosphoric acid (H₃PO₄) [20], can produce AC with well-developed pore morphology and enhanced phenol adsorption capacity. In addition, the introduction of some basic nitrogen-containing functional groups, such as amine, pyridinic, pyrrolic and quaternary nitrogen groups, will increase the higher π-electron density in basal plane of AC and thus lead to higher phenol adsorption [21]. The introduction of some basic nitrogen-containing functional groups can be realized by the exposure of AC to gaseous ammonia (NH₃) [22], urea (H₂NCONH₂) and melamine (C₃H₆N₆) [23]. It is needed to notice that the abovementioned activation methods are categorized into chemical activation and they always incorporate complex procedures compared with physical activation. In order to make a supplement to the physical activation research, a thermal modified method for AC was put forward in this work. The mechanism of thermal modification was elucidated based on porous structure and surface chemistry analyses. The kinetics, equilibrium and thermodynamics behaviors of phenol adsorption on the modified AC sample were also investigated.

2. Materials and Methods

2.1. Precursors and thermal modification of AC samples

The raw AC sample was obtained from coconut shell, which underwent carbonization and steam activation in turn. The thermal modification of raw AC sample was conducted in a muffle furnace. Raw AC sample was loaded in a closed crucible. The loaded crucible

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was heated isothermally for 1 h. In order to investigate the heating temperature dependence of phenol adsorption, three temperature points (700, 900 and 1100 °C) were studied. The raw and modified AC samples were crushed and sieved into diameters between 0.3 and 1.4 mm.

All the AC samples were preserved in sealed plastic containers, and helium (He) was injected to prevent undesired oxidation. Before each adsorption test, samples were dried at 105 °C for 24 h under vacuum condition.

2.2. Adsorption of phenol

Batch adsorption of phenol from the aqueous solutions were conducted at 25–55 °C by agitating 12 g of each AC sample with 1200 ml of phenol solution of desired concentration in a flat bottom flask. The flask was placed in a thermostatic shaker bath at 200 r·min⁻¹. In order to determine the phenol concentration, liquid sample was extracted and filtered. The phenol concentration of the pre-processed liquid sample was determined using a PUXI T6 UV–Vis ultraviolet spectrophotometer at a wavelength of 270 nm. Each experiment was carried out in duplicates and the arithmetic mean value was adopted as the final phenol concentration. The adsorption amount of phenol on AC sample at adsorption time (*t*), *q_t*, was calculated according to

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

where *q_t* (mg·g⁻¹) is the adsorption amount of phenol on AC sample at *t*; *V* (L) is the volume of the solution; *C₀* and *C_t* (mg·L⁻¹) are the initial phenol concentration and instantaneous phenol concentration corresponding to *t*, respectively; *m* (g) is the mass of AC sample.

The kinetics curves of phenol adsorption on various AC samples were generated by plotting *q_t* versus *t*.

When the adsorption reach equilibrium state, the equilibrium adsorption amount of phenol (*q_e*, mg·g⁻¹) was given by

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

where *C_e* (mg·L⁻¹) is the equilibrium concentration of phenol.

The adsorption isotherms of phenol adsorption on various AC samples were obtained by plotting *q_e* versus *C_e*.

2.3. Pore morphology of AC samples

The pore morphologies of AC samples were analyzed using the ASAP 2020, provided by Micromeritics instruments. Prior to pore morphology analysis, all the samples were degassed under vacuum for 12 h to effectively drive out the residual gas and moisture. The nitrogen adsorption and desorption isotherms at 77 K were collected at relative pressures (*p/p₀*) ranging from 0.005 to 0.995. In this work, the specific surface area, pore volume and pore size of each sample were analyzed based on the nitrogen adsorption and desorption data. Further calculative details can be found in [24].

2.4. Surface chemistry of AC samples

It has been pointed out that oxygen-containing functional groups have an important impact on phenol adsorption on carbon-based adsorbents [25–27]. And oxygen-containing functional groups usually occur in the form of carboxyl, phenolic hydroxyl and lactone base [28]. Thus, the amounts of the above groups on AC samples were determined by the frequently-used titration method proposed by Boehm [29].

In addition, Fourier Transform Infrared (FTIR) spectroscopy analysis using FTIR spectrometry (EQUINOX55, Bruker Corp., Germany) was also applied to determine the surface chemistry of the AC samples. All the samples and the dried KBr were ground at a mass ratio of 1:100. The FTIR spectra were generated with 32 scans at a resolution of 4 cm⁻¹.

2.5. X-ray diffraction analysis

X-ray diffraction (XRD) analysis using nickel-filtered Cu K_α radiation ($\lambda = 0.154056$ nm) was performed on Rigaku D/Max-2550PC at 40 kV and 200 mA. The scanned angle (2θ) was limited between 5° and 75° with step size 0.01°.

3. Results and Discussion

3.1. Thermal modification temperature

The modified AC samples obtained from 700 °C, 900 °C and 1100 °C together with the raw state were designated as AC₁, AC₂, AC₃ and AC₀, respectively. In order to primarily explore the phenol adsorption performance of all AC samples, adsorption experiment was carried out at temperature of 25 °C and initial phenol concentration of 1000 mg·L⁻¹. As shown in Fig. 1, it can be observed that the phenol adsorption of all the three AC samples after thermal modification is superior to the raw sample and the order of phenol adsorption is as follows: AC₂ > AC₁ > AC₃ > AC₀. In consideration of phenol adsorption on various modified AC samples, the optimum modification temperature is 900 °C, followed by 700 °C and 1100 °C.

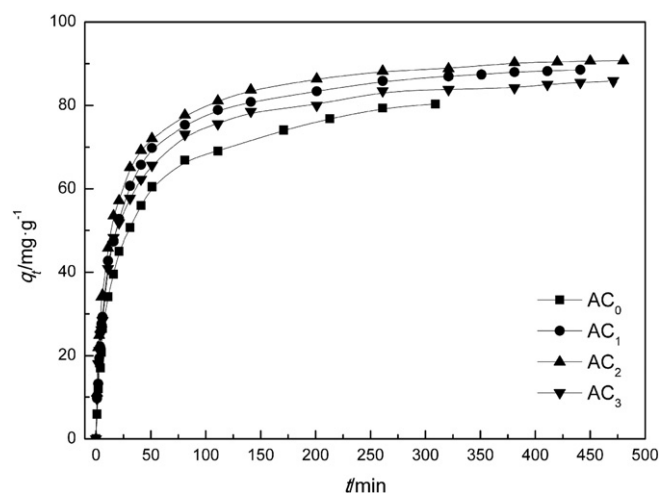


Fig. 1. Phenol adsorption curves of various AC samples.

3.2. Characteristics of AC samples

The nitrogen adsorption–desorption isotherms of four AC samples were shown in Fig. 2. In accordance with the classification approach of Brunauer, Deming, Deming, Teller (BDDT) [30], all the adsorption isotherms (adsorption branch) are categorized into type I isotherm which is described for microporous adsorbents. The hysteresis loop constituted by adsorption branch and desorption branch is also detected for each AC sample. The shape of the hysteresis loop can help to assess to the pore shape of the adsorbent [16]. Because slight difference is observed between the hysteresis loop of isotherms of the raw AC sample and the other three modified AC samples, it can be concluded that thermal modification method has a minimal effect on the pore shape of AC sample.

Based on the low temperature nitrogen adsorption and desorption data presented in Fig. 2, the pore morphology parameters of AC samples including specific surface area, pore volume and pore size were given in Table 1. It can be seen that the raw sample (AC₀) is a highly-developed micro–mesoporous carbon-based material with larger BET specific surface area, pore volume and smaller pore diameter in comparison with all the thermal modified AC samples. With the modification temperature increasing from 700 to 1100 °C, a degradation trend in pore morphology is observed. It is reported that the heat treatment will cause the expansion of microcrystalline structure of AC [31]. Therefore, it

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