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Adsorption kinetics of phenol in aqueous solution onto activated carbon from wheat straw lignin

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ABSTRACT

Activated carbon produced from wheat straw lignin using chemical activation with phosphoric acid acts as an activator at 873 K. Porous structure of activated carbon was characterized by scanning electron microscopy and nitrogen adsorption. The BET surface area of activated carbon is 1,123 m^2/g, the total pore volume is 0.43 cm^3/g, and the nominal pore size is 0.12 nm. Experiments were performed to investigate the adsorption kinetics of phenol in aqueous solution onto activated carbon. Four models (the pseudo-first-order model of Lagergren, the pseudo-second-order model of Lagergren, Elovich equation, and the intraparticle diffusion model) were used in this study. The results showed that the adsorption processes were perfectly fitted to the pseudo-second-order model with very high regression coefficients. The application of the intraparticle diffusion model indicated that the adsorption mechanism of phenol in aqueous solution was rather a complex process. The rate was controlled not only by intraparticle diffusion but also some other mechanisms.

Keywords: Adsorption kinetic; Phenol; Activated carbon; Wheat straw lignin

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1. Introduction

Industrial development has led to major problems of environmental pollution level. Large amounts of pollutants are released into bodies of water. Among various harmful and toxic pollutants, phenol is highly toxic and refractory [1]. Pollution of phenol is generated from various industrial processes and is harmful to the living organisms and the ecosystem [2]. Toxic effects of phenol on humans include anorexia, fainting, vomiting, liver damage, kidney damage, headache, coma, paralysis, and other serious mental problems [3]. Therefore, their treatment is very important for safe discharge.

Recently, various technical processes such as solvent extraction, biodegradation, adsorption, and chemical oxidation have been attempted for the removal or degradation of phenol from wastewater [4–6]. Among these water treatment methods, adsorption is preferred because it is of lower cost and highly efficient. Activated carbons as efficient adsorbents are widely applied to remove phenol from wastewater due to its high surface area, extensive adsorption capacity, and various surface functional groups [7]. However, its widespread use is extremely restricted by its high cost of production. Hence, the production of activated carbon from cheaper precursor has significant values.

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Extensive work has been carried out to find new activated carbons from many cheaper and renewable precursors [8–10].

There is a strong interest worldwide in developing suitable technologies that can derive chemicals and materials from renewable biomass. Numerous waste materials have been used successfully for the preparation of activated carbons including hazelnut shell, rice husk, waste tires, fruit stones, and municipal waste [11]. Lignin is one of the most abundant substances in nature. Because lignin is an aromatic macromolecule that is readily available and comparatively inexpensive, it may fulfill many of the requirements for being a precursor to the activated carbons. Using lignin as a renewable feedstock for fine chemicals and materials has the potential to generate significant environmental and economic benefits [12–16]. Lignin has proved its high content of carbon and its potential application for preparing carbonaceous adsorbents [17]. This solution can be considered as an alternative measure to dispose excess lignin and turn solid waste into valuable products in order to control environmental pollution [18].

In this work, the activated carbon is obtained from wheat straw lignin with H_3PO_4 activation. Then, the pore structure characteristics and adsorption phenol in aqueous solution capacity of the activated carbon were investigated. The adsorption kinetics of phenol in aqueous solution will be investigated and discussed.

2. Materials and methods

2.1. Preparation of the adsorbents

The wheat straw was obtained from Jinan in Shandong Province of P.R. China. The wheat straw was dried at 378 K for 12 h in order to achieve constant weight. In addition, the content of C, N, H, O, and ash in wheat straw was 52.66, 0.32, 6.83, 34.52, and 5.67%, respectively. Then, they were grounded and sieved into a uniform size of 100 meshes. The 50 g of the wheat straw was soaked stilly with 100 mL 55% H_3PO_4 solution in 250 mL Erlenmeyer flask for 2 h at room temperature. Then, it was dried again at 378 K for 12 h to constant weight and was carbonized at 873 K in a muffle furnace for 12 min. The product of 100 mesh activated carbon was thus obtained and then stored for later adsorption experiments.

2.2. Adsorption experiments

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flask containing 0.1 g of activated carbon and 100 mL 500 mg/L of phenol in aqueous solution. The initial pH in solution was adjusted to 4.0 with 1 mol/L H_2SO_4. The flasks were placed in a shaker at 308 K and 200 rpm. The samples were analyzed by UV–vis spectrophotometer at 279 nm wavelength.

2.3. Analytical methods

The textural characteristics of activated carbon including surface area, pore volume, pore size distribution were determined using standard N_2-adsorption techniques. The surface physical morphology of activated carbon was observed by a scanning electron microscope.

The amount of adsorbed phenol q_t (mg/g) at different time was calculated as follows:

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

where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of phenol, respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

2.4. Statistical analyses of data

All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean ± SD). All statistical significance was noted at $\alpha = 0.05$ unless otherwise noted.

3. Results and discussion

3.1. Characterization of activated carbon

Scanning electron microscopy has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. The surface of the activated carbon was observed using scanning electron microscopy as shown in Fig. 1. From Fig. 1, there is a good possibility for phenol in aqueous solution to be trapped and adsorbed into these pores. It can be seen from the micrograph that the activated carbon contains irregular and porous structures, indicating that activated carbon presents adequate morphology for phenol adsorption.

It is well known that the adsorption capacity of activated carbon can be recognized from their physical characteristics such as porosity, pore volume, surface area, and pore size. The N_2 adsorption isotherm curves were conducted to reflect these physical characteristics.

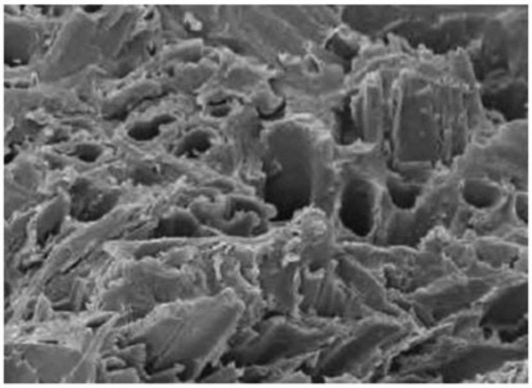

Fig. 1. SEM image of activated carbon.

The textural characteristics of activated carbon are obtained from the standard N_2-adsorption techniques. The adsorption and desorption isotherms of the activated carbon are shown in Fig. 2. It can be seen that the isotherms were reversible, indicated simultaneous presence of micropores and mesopores. It exhibited relatively obvious high adsorption capacities.

The specific surface area and pore structure of the activated carbons are measured. The BET surface area of activated carbon is 1,123 m^2/g, the total pore volume is 0.43 cm^3/g, and the nominal pore size is 0.12 nm. It shows that activated carbon has a large specific surface area typical for commercial activated carbons [19].

3.2. Effect of contact time

The influence of contact time on the removal of phenol in aqueous solution by activated carbon is shown in Fig. 3. It can be concluded that the adsorption process is very rapid. The adsorption rate of phenol increases sharply at short contact time and slowed gradually as equilibrium was approached. It may be due to the availability of initial large number of vacant surface active sites for adsorption and adsorption rate is very fast. As equilibrium was approached, the filling of vacant sites becomes difficult due to repulsive forces between phenol adsorbed on solid surface and phenol from solution [20].

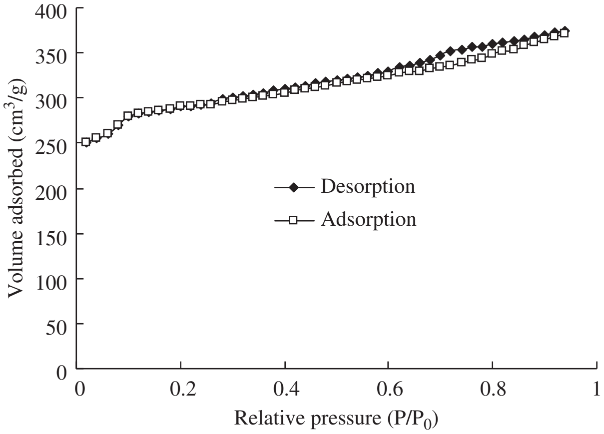

Fig. 2. N_2 adsorption–desorption isotherms of activated carbon at 77 K.

3.3. Adsorption kinetics

In order to investigate the adsorption kinetic mechanism of phenol in aqueous solution onto activated carbon, four models (the pseudo-first-order model, the pseudo-second-order model, the Elovich equation, and the intraparticle diffusion model) were used in this study.

The linear pseudo-first-order model of Lagergren is given as follows [21]:

$$\ln\,(q_e - q_t) = \ln q_e - k_1 \times t \tag{2}$$

where q_e and q_t are the amounts of phenol absorbed onto the adsorbent (mg/g) at equilibrium and at t, respectively. k_1 is the rate constant of first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model developed by Ho and McKay [22] is based on the experimental information of solid-phase sorption. The linear pseudo-second-order model can be expressed as follows:

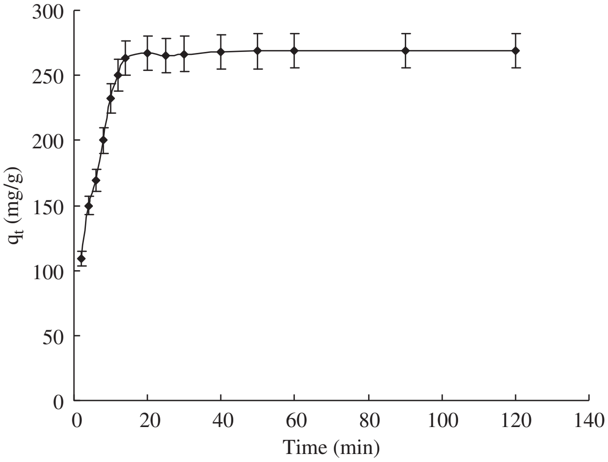

Fig. 3. Effect of contact time on adsorption of phenol in aqueous solution onto activated carbon. Experimental conditions: 0.10 g of activated carbon, 500 mg/L of initial phenol concentration, 308 K, 200 rpm, and pH 4.0.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 is the rate constant of second-order adsorption (g/mg min).

The Elovich equation is used for general application to chemical adsorption [23]. The equation has been applied satisfactorily to some chemical adsorption processes and has been found to cover a wide range of slow adsorption rates. The same equation is often valid for systems in which the adsorbing surface is heterogeneous, and is formulated as:

$$q_t = \left(\frac{1}{\beta}\right) \times \ln(\alpha \times \beta) + \left(\frac{1}{\beta}\right) \ln(t) \tag{4}$$

where α is the chemical adsorption rate (mg/mg min) and β is a coefficient in relation with the extension of covered surface and activation energy of chemical adsorption (g/mg). The equation constants are tabulated from the plot of the straight line q_t vs. $\ln t$.

According to Hamdaoui [24], any kinetic approach of the intraparticle diffusion may be deduced successively from works of Weber and Morris [25] and Boyd et al. [26]. As proved recently [27], in order to appreciate the role of the intraparticle diffusion in the adsorption process, the following kinetic expression is used:

$$q_t = k_i t^{\frac{1}{2}} \tag{5}$$

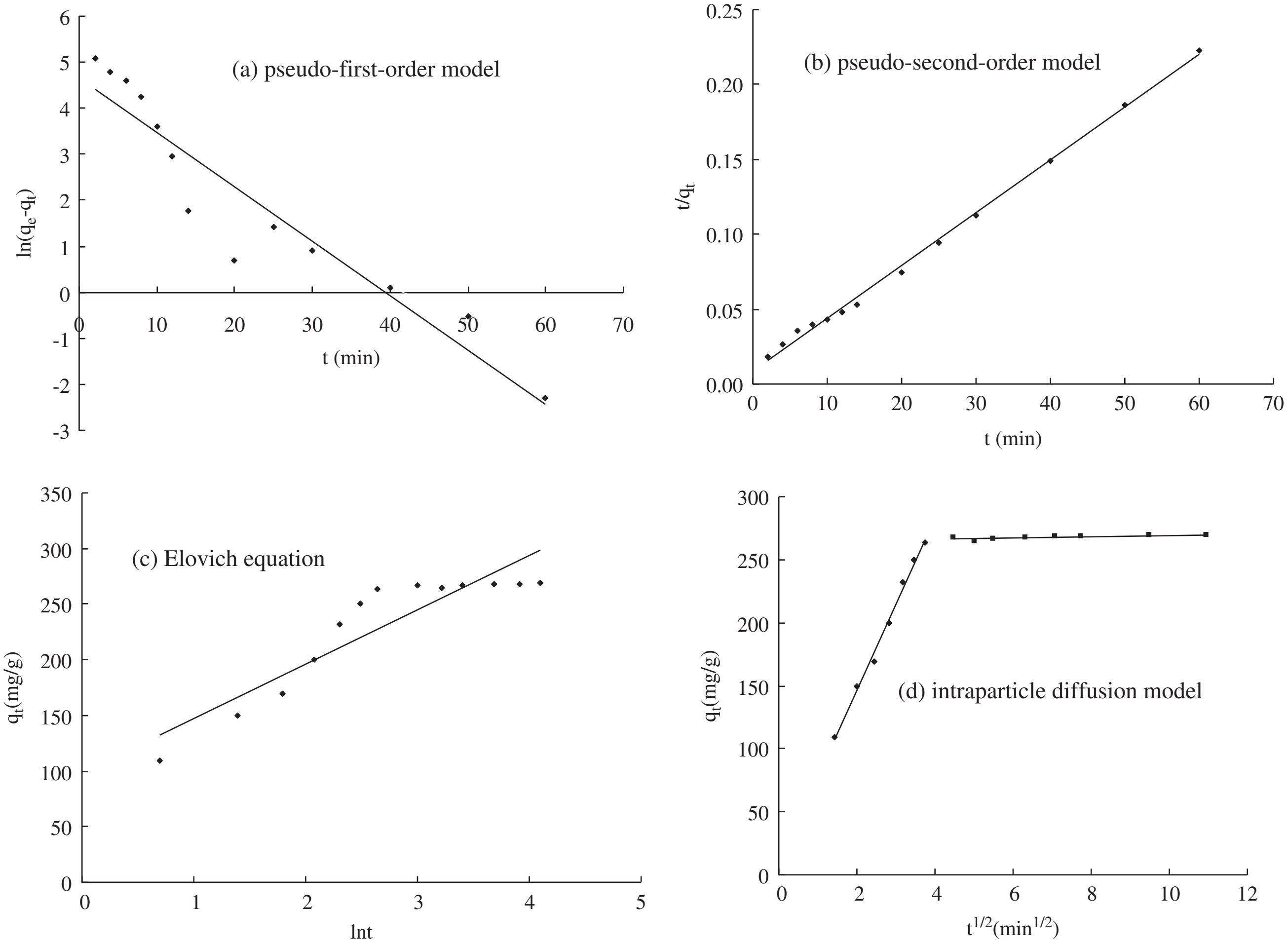

Fig. 4. (a) Pseudo-first-order model for adsorption of phenol in aqueous solution onto activated carbon at 308 K. (b) Pseudo-second-order model for adsorption of phenol in aqueous solution onto activated carbon at 308 K. (c) The Elovich equation for adsorption of phenol in aqueous solution onto activated carbon at 308 K. (d) Intraparticle diffusion model for adsorption of phenol onto activated carbon at 308 K.

Experimental conditions: 0.10 g of activated carbon, 500 mg/L of intial phenol concentration, 200 rpm, and pH 4.0.

Table 1
Kinetic parameters for the adsorption of phenol in aqueous solution on activated carbon. Experimental conditions: 0.10 g of activated carbon, 500 mg/L of initial phenol concentration, 308 K, 200 rpm, and pH 4.0

Pseudo-first-order			Pseudo-second-order			Elovich equation		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/(mg min))	R^2	α (mg/(mg min)	β (g/mg)	R^2
105.6150	0.1184	0.8998	285.7143	1.346×10^{-3}	0.9974	365.0847	0.02042	0.8381

or

$$q_t = k_i t^{\frac{1}{2}} + C_{st} \tag{6}$$

where k_i and C_{st} are the constant of intraparticle diffusion rate. It can be obtained from the slope of the straight line of q_t vs. $t^{\frac{1}{2}}$.

The adsorption kinetic models were shown in Fig. 4.

All kinetic data for the adsorption of phenol in aqueous solution onto activated carbon could be derived from this line. In Table 1, the parameters were listed about the pseudo-first-order model (q_e and k_1), the pseudo-second-order model (q_e and k_2), and the Elovich equation (α and β). The validity of the exploited models is verified by the correlation coefficient (R^2). R^2 values of the pseudo-first-order model, the pseudo-second-order model, and the Elovich equation for adsorption of phenol in aqueous solution onto activated carbon were 0.8998, 0.9974, and 0.8381, respectively. If the reaction of desorption is neglected, this model of the pseudo-first-order expresses the proportionality between the reaction rate and the aqueous phenol concentration. It was found that this model was not suitable for activated carbon system. Meanwhile, the Elovich equation for adsorption of phenol in aqueous solution onto activated carbon was also not suitable. Comparison of the R^2 values for different models suggests that the pseudo-second-order kinetic model fits best because of its highest value. The pseudo-second-order kinetic model implies that the predominant process here is chemical adsorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent [28,29].

The adsorption kinetics may alternatively be described from a mechanistic point of view. The overall adsorption process may indeed be controlled either by one or more steps, such as external diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface, or a combination of more than one step. The intraparticle diffusion model was tested to identify the diffusion mechanism which was not identified by the pseudo-second-order model. Plot of quantity of phenol in aqueous solution adsorbed against square root of time is given in Fig. 4(d).

It indicated that the plots were not linear over the whole time range and the adsorption process was influenced by two stages. The first stage could be attributed to adsorption of phenol over the surface of the resin beads, and therefore it was the fast adsorption stage. The second stage was the equilibrium phase and might be regarded as the diffusion through mesopores and micropores. In this stage, it was a controlled rate step followed by the achievement of equilibrium. It can also be observed that the lines did not go through the origin and the second stage of phenol adsorption did not follow the Weber–Morris equation [25]. The adsorption mechanism is rather a complex process and the intraparticle diffusion was not the only controlled rate step. The rate was controlled not only by intraparticle diffusion but also by some other mechanisms, such as boundary layer control [7,30].

4. Conclusions

The activated carbon was obtained from wheat straw lignin with H_3PO_4 activation. Then, the pore structure characteristics and adsorption phenol in aqueous solution capacity of the activated carbon were investigated. The activated carbon contains irregular and porous structures and a large specific surface area. The adsorption of phenol in aqueous solution onto activated carbon is fast and the adsorption kinetics can be best described by the pseudo-second-order model. The adsorption mechanism of phenol in aqueous solution was rather a complex process. The rate was controlled not only by intraparticle diffusion but also by some other mechanisms.

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