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Absorption of Phenol on Nitrogen-Enriched Activated Carbon from Wood Fiberboard Waste with Chemical Activation by Potassium Carbonate

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Abstract

Preparation of nitrogen-enriched activated carbons from wood fiberboard waste was studied. Activated carbons were obtained with an impregnation ratio (gram chemical agent/gram wood fiberboard waste) of 3 with 50 % potassium carbonate solution in 800°C activation temperature carbonized for 1h. Optimum adsorption conditions were determined as a function of effects of contact time, pH, and dosage of activated carbon and temperature of solution for phenol adsorption. Adsorption equilibrium was achieved with in 120 min at the given phenol concentration of 250 mg/L. When 0.3 g of the carbon absorbent and 100 mL of phenol solution at 250 mg/L were used, maximum adsorption capacity of phenol on activated carbon can reach 208 mg/g. In the adsorption isotherm .the Langmuir model fit better than the Freundlich model in phenol adsorption. The kinetics of phenol adsorption followed nicely the pseudo-second-order rate expression.

Keywords: Phenol adsorption; Activated carbon; Wood fiberboard waste

Introduction

Phenols are pollutants of high priority concerns because of their toxicity and possible accumulation in the environment. Phenols are introduced into surface water from industrial effluents such as those from the coal tar, gasoline, plastic, rubber proofing, disinfectant, pharmaceutical and steel industries and domestic wastewaters, agricultural run-off and chemical spills. Various methods have been proposed for the treatment of wastewaters containing organic and inorganic pollutants. These processes are based on the principles of precipitation and coagulation, chemical oxidation, sedimentation, filtration, adsorption, osmosis, ion exchange, etc. [1,2].

Adsorption technology has been widely studied for removal of organic and inorganic micro pollutants from aqueous solutions. There are many absorbents in use. Activated carbon is the most widely used for the removal of a variety of organics from waters, but the disadvantage associated with it is the high regeneration cost, due to the use of nonrenewable and relatively expensive starting material such as coal, a major economic consideration. This has prompted a growing research interest in the production of activated carbons from locally available materials especially for application concerning waste wood [3]. Several wood processing residues and agricultural residues have been found to be suitable precursors for production of activated carbon. Because the biomass obtained from these materials are cheaper, renewable and abundantly available and have high carbon and low ash contents [4].

In the past few years, enhanced adsorption capacity toward phenol on activated carbons has currently receiving great attention [5,6]. Because introducing nitrogen-containing surface group makes activated carbon more alkaline, increased adsorption of acidic agents is expected. Therefore, nitrogen-enriched activated carbon could increase ability to adsorb phenolic compounds [7]. However, nitrogen content in commercially used activated carbon is very low. There are several methods for preparing activated carbon with enhanced levels of nitrogen. The methods used for the synthesis of nitrogen-containing porous carbons can be divided into two groups. First, it is the treatment of conventional activated carbon at an elevated temperature with ammonia, ammonia-air or ammonia-steam mixtures [8-10]. The second approach consists in the condensed phase pyrolysis of nitrogencontaining precursors [11-13] or co-pyrolysis of suitable nitrogen carrier with a common carbon precursor, followed by the activation of the resultant chars [14-17]. Among above-mentioned methods for making nitrogen-containing activated carbon, it is quite necessary to find more cost-effective ways of production. There is great potential for developing activated carbon products from wood waste. In waste wood fiberboard, nitrogen is introduced to the wood matrix from the use of nitrogen containing amino plastic adhesives such as urea-formaldehyde and melamine-formaldehyde resins. Nitrogen-containing adhesives are dispersed through wood fiberboard. Accordingly, preparation of nitrogen-enriched activated carbon from waste wood and its adsorption behavior on phenol would be an interesting research subject.

The aim of this work is to illustrate adsorption of phenol on nitrogenenriched activated carbon prepared from wood fiberboard waste. A series of important factors such as contact time, adsorbent dose, pH, and temperature were investigated. Also, adsorption isotherms and adsorption kinetic studies were reviewed.

Materials and Methods

Materials

Waste fiberboard (WFB) was provided by Beijing Forestry University wood factory. WFB consisted of poplar wood and urea–formaldehyde resin (10 %).Phenol, Potassium carbonate (K_2CO_3) and hydrochloric acid (HCI) were analytical grade and were purchased from Beijing

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Lanyi chemical (Beijing, China). Double distilled water was used for preparation of all required solutions.

Preparation of the activated carbons

The preparation of activated carbon is divided into two steps. The first step is carbonation, WFB was cut into $250 \times 20 \times 5$ mm pieces, There pieces were heated to a carbonization temperature of 500° C at a heating rate of 100° C/h and were maintained at this temperature for 1 h. The samples were then grounded and screened with sieves. The fraction in the particle diameter ranged from 40-60 mesh. Particle samples were dried in a105°C oven for 4 h.

In the activation step, 3 g of oven-dried samples was soaked in 50 % K_2CO_3 solution for 16 h at the investigated impregnation (gram chemical agent/gram WFB waste) of 3. The soaked samples were then put in an electric furnace and heated up to about 800°C at a heating rate of 10°C /min⁻¹.Samples were held at this temperature for 50 min before cooling down and followed by washing sequentially with a 0.5 N HCI solution. Activated carbons were repeatedly washed with hot distilled water until pH of the solution reached about 6-7. Finally, these activated carbons were dried in the 105°C oven for 4 h.

Phenol adsorption process

Adsorption kinetics and equilibrium studies were conducted at ambient temperature. A known amount of the adsorbent was put in flasks containing100 mL of aqueous phenol solution at predetermined concentration [18]. The flasks were hermetically closed, not only for avoiding the loss of phenol by volatilization, but also for preventing the entry of oxygen, which is known to lead to irreversible phenol adsorption through oxidative coupling [19]. Then the flasks were shaken for 100 min. At the end of the adsorption process, adsorbent particles were filtered out using 0.45 mm membranes. The residual phenol concentration was measured by UV absorption in a UV-2102c spectrophotometer (Unico, USA) with a wavelength of λ max=270 nm [20].

The amount of adsorption at equilibrium, $q_{_e}({\rm mg/g}),$ was calculated by:

Fiberboard	Properties	Activated carbon from WFB		
1	C content (wt %)	90.46		
2	H content (wt %)	0.59		
3	N content (wt %)	1.36		
4	lodine number (mg/g)	1370		
5	BET surface area (m ² /g)	1576		
6	Total pore volume (cm ³ /g)	0.953		

WFB, waste fiber board; BET, Brunauer-Emmett-Telle

Table 1. Characteristics of activated carbon from fiberboard.



$$q_e = (c_0 - c_e) \times v/w \tag{1}$$

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Where c_0 and c_e (mg/L) are the concentrations of phenol at initial stage and equilibrium stage, respectively. *V* is the volume of the solution (L) and *w* is the mass of adsorbent used (g).

Results and Discussion

Characteristics of the as-prepared activated carbons

The properties of the prepared activated carbon were determined by standard methods as summarized in Table 1. Elemental analysis (contents in carbon, hydrogen and nitrogen) of the prepared activated carbon w as made in a CHNS analyzer (Flash, EA.1112 series, Thermo Finnigan San Jose, CA). Iodine number was determined at 303 K based on ASTM D4607-94 (ASTM 2011). Pore structure characteristics of activated carbon were measured by N₂ adsorption isotherm at -196°C using an ASAP 2010 analyzer (Micro meritic Norcross, GA). The Brunauer-Emmett-Teller (BET) surface areas were calculated from N₂ adsorption isotherms by using the BET equation.

Effect of contact time

The 0.1 g activated carbon sample was put into 250 mL flasks containing 100 mL of buffered aqueous phenol solution. The initial concentration of phenol was 250 mg/L. The result is shown in Figure 1.

Adsorbent were filled and the adsorption of phenol became slower gradually and reached a plateau. The phenol removals versus time curves were single, smooth and continuous leading to saturation, suggesting the possible monolayer coverage of phenol on the surface of the adsorbents [21].

In this experiment, the equilibrium time was 120 min, which the maximum surface areas were obtained with the activation of 50 % K_2CO_3 impregnated samples as 1576 m²/g. meantime, the capacity of the activated carbon from WFB was 208 mg/g and the phenol removal could get 83 %. Tancredi et al. [22] reported that phenol adsorption capacity of activated carbon from Eucalyptus wood was 64 mg/g in 750 min and phenol removal could reach 32%. In a study reported by Mohanty et al. [23], capacity of activated carbon from Sterculia alata nutshell could reach 140 mg/g and phenol removal achieved 80% in 300 min. Compared with results reported in these two studies, phenol removal was higher and equilibrium time shorter in this study. Because introduction of nitrogen-containing surface groups made activated carbon more alkaline, increased adsorption of phenol was expected.

Since the adsorption rate became constant at about 120 minutes, there was no significant growth in the adsorption when the contact time increased from 120 minutes to 180 minutes. Therefore, the optimum contact time for all the further experiments was set as 120 min.

Effect of dosage of activated carbon

For investigating of effect of adsorbent dosage on adsorption, the experiments were conducted with the initial concentration of phenol was maintained at 250 mg/L and samples having different adsorbent dosage ranging from 0.01 to 0.30 g (0.01 g, 0.02 g, 0.05 g, 0.15 g 0.20 g 0.25 g 0.30 g) in 100 mL unbuffered aqueous phenol solution. The result was illustrated in Figure 2.

It could be observed from the Figure 2. At the dosage of activated carbon level is 0.25 g, the phenol adsorption dose is at its maximum, and then as dosage of active carbon increased, the unit



nol concentration = 250 mg/L, equilibration = 120 min).



Figure 3: Effect of temperature on adsorption of phenol (carbon dosage = 0.1 g; phenol concentration = 250 mg/L; equilibration time = 120 min).



adsorption volume has dropped significantly. The phenol removal a sharp drop as the adsorbents dose increased. When the adsorbent dose further increased from 0.1 g to 0.3 g, a significant increase in phenol adsorption was observed. In any case, because introducing nitrogen-containing surface groups makes activated carbon more alkaline. The increase in the percent adsorption of phenol was due to the availability of larger surface area with more active functional groups [24]. As a result, the optimum dosage of activated carbon was 0.25g.

Similar phenomenon was also observed by Murat Kilic et al. [25], reported that that the adsorption behavior of phenol onto two carbons are generally similar. The adsorption capacity increased with increasing adsorbent amount and then became constant indicating that 0.2 and 0.4 g/L were sufficient for the optimum removal of phenol from aqueous solution, respectively. Therefore, the dosages of 0.2 and 0.4 g/L were used for the following phenol adsorption experiments.

Effect of temperature

The adsorptions of phenol on activated carbon removal as a function of temperature value were verified in the range of 20-45°C.

The initial concentration of phenol was 250 mg/L and the contact time for adsorption was kept at 120 min to ensure the complete equilibrium. The result was seen in the Figure 3.

With the temperature varied from 20°C to 35°C, the phenol removal slowly increased, and as the temperature further increased from 35°C to 40°C, the phenol removal rate increased from 38.47 % to 47.05 %. In the paper, the adsorption capacities of 90.00, 96.18, 117.64 and 106.73 mg/g were reported at 20, 35, 40, 45 °C respectively. Similar phenomenon was also shown by Karabacakoglu et al. [26], Hazelnut Bagasse carbon activated with zinc chloride was examined for the removal of phenol from water. The results showed that the adsorption capacities of 97.36, 91.32 and 99.27 mg/g were found at 25, 35 and 45°C respectively. Compared with results reported by Karabacakoglu et al. [26] and in this paper, phenol removal was higher at the same temperature. The reason was that introduction of nitrogen-containing surface groups made activated carbon more alkaline, increased adsorption of phenol was expected.

As the temperature further increased beyond 40°C, the phenol removal rate decreased sharply. The result indicated that the maximum adsorption for phenol was obtained at 40°C for the activated carbon prepared from WFB.

Effect of pH

The effect of pH on the equilibrium adsorption of phenol on prepared activated carbon was examined over a pH range of 4-9. The initial concentration of phenol was 250 mg/L and the adsorbent dose was 0.1 g. The pH of unbuffered aqueous phenol solution was 7.0, and then pH values were adjusted with 0.1 M HCI and 0.1 M K₂CO₃

Figure 4 is show that the maximum removal of phenol at the given absorbent dosage and given phenol concentration is observed at pH of 7.0 and adsorption capacity was 208mg/g. The potential of nutshells of Sterculia alata, a forest waste to prepare activated carbons by zinc chloride activation to remove phenol from aqueous solution was evaluated Mohanty et al. [23] Results were shown that the maximum uptake of phenol was found at pH 3.5 and adsorption capacity was 2.8 mg/g.

This trend could be explained considering the nature of the adsorbent at different pH in phenol adsorption. Due to the phenol itself is soluble in acidic water solution (pKa=9189), and phenol in acidic or neutral aqueous solution exists mainly in molecular state, with affinity is bigger, the surface of activated carbon to adsorption; While in alkaline aqueous solution exists mainly in ion state, large and is not conducive to the affinity adsorption with water. When the pH>7, dissociation forms of phenol are more likely to be soluble in solution, and only binding force strong chemical bonds between adsorption and water is broken, only possible adsorption, dissociation and activated carbon adsorption in the form of the increase of repulsion between the surface also increases the adsorption force of smaller. In the higher pH range phenol forms salts which readily ionize leaving negative charge on the phonetic group. At the same time the presence of OH- ions on the adsorbent prevents the uptake of phenol [27,28]. Therefore, the optimum pH was 7.0.

Adsorption isotherm

The Langmuir and Freundlich models were the most common models to describe the adsorption isotherms.

Langmuir adsorption isotherm was given by the following equation [28].

$$c_{e}/q_{e} = 1/(q_{m} \times b) + (1/q_{m}) \times c_{e}$$
 (2)





La	Freundlich				
qm (mg/g)	В	R²	n	K _f	R²
213,46	0.23	0.93	3. 51	64.05	0.96

 Table 2: Parameters of different isotherms of adsorption of phenol on activated carbon.

Where q_m (mg/g) is the amount of adsorption corresponding to complete monolayer coverage and *b* (1/mg) is the Langmuir constant related to the energy or net enthalpy of adsorption. The linear plots of c_e/q_e versus c_e were shown in Figure 5.

Freundlich adsorption isotherm was given by the following equation [29].

$$q_e = K_f C_e^{1/n} \tag{3}$$

Where K_j and n are Freundlich constants related to adsorption capacity and adsorption intensity. Usually, for a good adsorbent 1<n<10. The phenol adsorption isotherm followed the linearized Freundich model as shown in Figure 6.

The values of Langmuir and Freundlich constant obtained were given in Table 2. Table 2 Parameters of different isotherms of adsorption of phenol on activated carbon. It could see that the Langmuir model fitted the results better then the Freundlich model. Since the value of 1/n was less than 1, it indicated a favorable adsorption. Similar trends were found in the article of Fierro et al. [5], which the Langmuir fitted better in the adsorption of phenol.

Adsorption kinetic studies

The rate constant of adsorption was studied under the pseudo-firstorder equation and the pseudo-second-order equation.

The pseudo-first-order equation was represented by the following equation.

$$\ln(q_e - q) = h \ q_e - k_1 \times t \tag{4}$$

Where q (mg/g) is the amount of phenol absorbed at time t (min); q_e (mg/g) is the amount of phenol absorbed at equilibrium and k_1 (1/min) is the first-order adsorption rate constant. The linear plot of $\ln(q_e$ -q) $\vee t$ was shown in Figure 7.

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The pseudo-second-order equation [30] based on equilibrium adsorption was expressed as:

$$t/q = 1/(k_2 \times q_e^2) + t/q_e$$
(5)

Where k_2 (g.mg.min-¹) is the rate constant of second-order adsorption. Also, the linear plot was shown in Figure 8.

The constants and R^2 values obtained from the two linear plots were summarized in Table 3.

The correlation coefficients R^2 , showed that the pseudo-second-order equation was more suitable for the experimental data. The data shows that good agreement between the experimental and the calculated q_e values was observed by using the pseudo-second-order equation. As a result, it is concluded that the adsorption of phenol on the activated carbon prepared from WFB follows the pseudo-second-order model. This may be expected that the overall rate of the adsorption process was controlled by chemisorptions [31].

Conclusion

The study results showed that the nitrogen-enriched activated carbon made from chemical activation of WFB with K_2CO_3 , which had a significantly higher phenol adsorption capacity contrasted with other non-nitrogen containing activated carbon. Compared to a series effects of contact time; pH, dosage of activated carbon, and temperature on





	Pseudo-second-order equation		
q ^e (mg/g) k ₁ (min ⁻¹) R ²	$q^{e}(mg/g) = k_{2}(g. mg.min^{-1}) = R^{2}$		
208.36 0.03 0.94	208.37 0.0070 0.99		

 Table 3: Parameters of different adsorption rate of phenol on activated carbon.

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phenol adsorption capacity of activated carbons; we concluded that the phenol removal became higher and the equilibrium time was shorter. Because introducing of N-containing surface groups made activated carbon more alkaline, increased adsorption of phenol was expected. The kinetics of phenol adsorption rate followed the pseudo-secondorder, and the Langmuir model fitted better than Freundlich model in phenol adsorption in the study of adsorption isotherm.

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