# PHENOL ADSORPTION ON NITROGEN-ENRICHED ACTIVATED CARBON FROM WOOD FIBERBOARD WASTE

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**Abstract.** Nitrogen-enriched activated carbons were prepared from wood fiberboard waste using 50% potassium hydroxide solution. Activated carbons were obtained with an impregnation ratio (gram chemical agent/gram wood fiberboard waste) of 3 in 850°C activation temperature carbonized for 60 min. Nitrogen content in activated carbon was 1.33% by analysis. Effects of contact time, pH, adsorbent dosage level, and temperature on phenol adsorption capacity of activated carbons were investigated. Adsorption equilibrium was achieved within 100 min at the given phenol concentration of 250 mg/L. When 0.1 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 207 mg/g. The kinetics of phenol adsorption followed nicely the pseudo-second-order rate expression. In the adsorption isotherm, the Langmuir model fit better than the Freundlich model in phenol adsorption. This study suggests that nitrogen-enriched activated carbon prepared from wood fiberboard waste can be used effectively for removal of phenol compounds from aqueous solutions.

*Keywords:* Activated carbon, wood fiberboard waste, phenol adsorption.

## INTRODUCTION

Phenol is a very common pollutant. It is becoming an increasing concern and may adversely affect human health and aquatic life. Phenol and phenolic compounds have low allowable limits (0.5-1.0 mg/L) because of their toxicity to human and aquatic life and must be removed from wastewaters in environmentally acceptable ways (Polat et al 2006).

Adsorption technology has been widely studied for removal of organic and inorganic micropollutants from aqueous solutions. The most widely used substance for removal of a variety of organics from water is activated carbon. However, the cost of generation and regeneration of activated carbon is relatively high. In 2006, average cost for producing activated carbon from the

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major producers was close to US $2500 per metric ton (Polat et al 2006). Worldwide demand is expected to expand 5.2% per year through 2012 to 1.2 million tons (Freedonia Group Inc 2008).

Enhanced adsorption capacity toward phenol was confirmed to occur on activated carbons of a basic nature regardless of textural characteristics (Ania et al 2002). In any case, because introducing nitrogen-containing surface groups makes activated carbon more alkaline, increased adsorption of acidic agents is expected. Therefore, nitrogen-enriched activated carbon could increase ability to adsorb phenolic compounds (Przepiórski 2006). However, nitrogen content in commercially used activated carbon is very low. There are several methods for preparing activated carbon with enhanced levels of nitrogen. One of the methods is carbonization followed by activation using nitrogen-containing plastics (Lahaye et al 1999). Another method of producing nitrogen-enriched activated carbon is exposure of preliminary activated carbon to nitrogen compounds in elevated temperatures (Jansen and Bekkum 1994; Bagreev et al 2004). A very effective process of nitrogen introduction into carbons is ammoxidation (Jurewicz et al 2004; Pietrzak et al 2007).

Although there are currently many methods for making nitrogen-containing activated carbon, there is always a need to find more cost-effective ways of production. There is great potential for developing activated carbon products from wood waste. According to statistics of the City Environment Protection Bureau, 6 billion tons of waste are generated in Chinese cities each year, and waste wood accounts for approximately 1%, which is about 60 million tons (Caturla et al 1991; Girods et al 2009). Most waste wood is burnt, which could release toxic gases and pollutants to the environment. In waste wood fiberboard, nitrogen is introduced to the wood matrix from the use of nitrogen-containing aminoplastic adhesives such as urea–formaldehyde and melamine–formaldehyde resins. Nitrogen-containing adhesives are dispersed through wood fiberboard. Therefore, preparation of nitrogen-enriched activated carbon

from waste wood and its adsorption behavior on phenol would be an interesting research subject.

The objective of this study was to evaluate adsorption of phenol on nitrogen-enriched activated carbon prepared from wood fiberboard waste. Several important factors such as contact time, adsorbent dose, pH, and temperature were investigated. Also, adsorption isotherms and adsorption kinetic studies were reviewed.

## MATERIAL AND METHODS

### Materials

Waste fiberboard (WFB) was collected from a wood processing factory at Beijing Forestry University. WFB consisted of poplar wood and urea–formaldehyde resin (12%). Phenol, potassium hydroxide (KOH), and hydrochloric acid (HCl) were analytical grade and were purchased from Beijing Lanyi Chemical (Beijing, China). Double distilled water was used for preparation of all required solutions.

### Preparation of Activated Carbon

Activated carbon was prepared using a two-step process. In the carbonization step, WFB was cut into $200 \times 10 \times 3$-mm pieces. These pieces were heated to a carbonization temperature of $500°C$ at a heating rate of $100°C/h$ and were held at this temperature for 1 h. The samples were then ground and screened with sieves. The fraction in the particle diameter ranged from 40-60 mesh. Particle samples were dried in a $105°C$ oven for 4 h.

In the activation step, 3 g of oven-dried samples was soaked in 50% KOH 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 $850°C$ 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 HCl 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 an 105°C oven for 6 h.

## Phenol Adsorption Process

Adsorption kinetics and equilibrium studies were conducted at ambient temperature. A known amount of the adsorbent was put in flasks containing 100 mL of aqueous phenol solution at predetermined concentration (Mohanty et al 2005). The flasks were hermetically closed to avoid loss of phenol during volatilization and to prevent entry of oxygen, which is known to lead to irreversible phenol adsorption through oxidative coupling (Terzyk 2007). Then the flasks were shaken for 100 min. At the end of the adsorption process, adsorbent particles were filtered out using 0.45-μm membranes. The residual phenol concentration was measured by UV absorption in a UV-2102c spectrophotometer (Unico, USA) with a wavelength of λmax = 270 nm (Bimer et al 1998).

Amount of adsorption at equilibrium, $q_e$ (mg/g), was calculated by

$$Q_e = (C_0 - C_e) \times V/W \qquad (1)$$

where $C_0$ and $C_e$ (mg/L) are concentrations of phenol at initial stage and equilibrium stages, respectively. V is volume of the solution (L), and W is mass of adsorbent used (g).

### RESULTS AND DISCUSSION

## Characteristics of Adsorbent

Elemental analysis (contents in carbon, hydrogen, and nitrogen) of the prepared activated carbon was 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 $N_2$ adsorption isotherm at –196°C using an ASAP 2010 analyzer (Micromeritic, Norcross, GA). The Brunauer-Emmett-Teller (BET) surface areas were calculated from $N_2$

Table 1. Characteristics of activated carbon from fiberboard.

| No. | Properties | Activated carbon from WFB |
|---|---|---|
| 1 | C content (wt%) | 90.44 |
| 2 | H content (wt%) | 0.57 |
| 3 | N content (wt%) | 1.33 |
| 4 | Iodine number (mg/g) | 1350 |
| 5 | BET surface area (m²/g) | 1876 |
| 6 | Total pore volume (cm³/g) | 0.949 |

WFB, waste fiber board; BET, Brunauer-Emmett-Teller.

adsorption isotherms by using the BET equation. Results are shown in Table 1.

## Effect of Contact Time

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

It can be seen from Fig 1 that adsorption of phenol on activated carbon increased with time and attained equilibrium in 100 min. In the beginning, the phenol adsorbed selectively occupied the active sites on the adsorbent. As contact time increased, the active sites on the adsorbent were filled and adsorption of phenol became gradually slower and reached a plateau. The phenol removal vs time curves were single, smooth, and continuous leading to saturation, suggesting possible monolayer coverage of phenol on the surface of the adsorbents (Namasivayam and Ranganathan 1995).

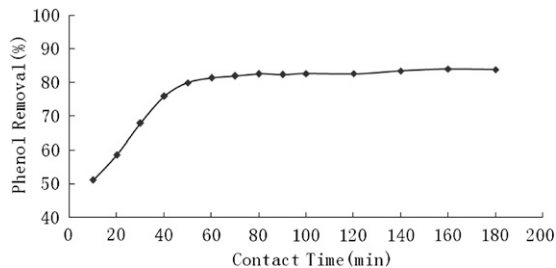In this study, equilibrium time was 100 min, capacity of activated carbon from WFB was



Figure 1.   Effect of contact time on adsorption of phenol (carbon dosage = 0.1 g; phenol concentration = 250 mg/L).

207 mg/g, and phenol removal was as high as 83%. Tancredi et al (2004) 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 (2006), 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.

Because adsorption rate became constant at about 100 min, there was no significant increase in adsorption when contact time increased from 100 to 180 min. As a result, optimum contact time for all further experiments was set at 100 min.

### Effect of pH

Initial phenol concentration was 250 mg/L, and the adsorbent dose was 0.1 g. The pH of unbuffered aqueous phenol solution was 6.5. pH values were adjusted with 0.1 M HCl and 0.1 M sodium hydroxide (NaOH). Effect of pH on equilibrium adsorption of phenol on prepared activated carbon was examined across a pH range of 4-9.

Effect of solution pH on adsorption capacity is demonstrated in Fig 2. It was evident that maximum removal of phenol at the given absorbent dosage and given phenol concentration was observed at 6.5 pH.
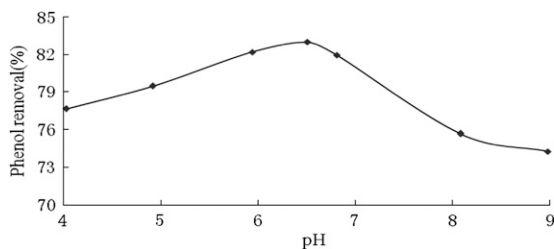
This phenomenon could be explained by the nature of the adsorbent at different pH in phenol adsorption. At lower pH values, uptake of phenol was less because of the presence of $H^+$ ions suppressing phenol ionization. Therefore, its uptake on polar adsorbent was decreased. In the higher pH range, phenol forms salts that readily ionize leaving negative charge on the phenolic group. At the same time, the presence of $OH^-$ ions on the adsorbent prevents uptake of phenolate ions (Rengaraj et al 1994; Singh et al 1994). Therefore, optimum pH was 6.5.

Similar trends of pH effect were also found from adsorption of phenol on activated carbon prepared from Tamarind Nutshell (Vaibhav et al 2005) and on activated carbon prepared from Tectona grandis sawdust (Mohanty et al 2005).

### Effect of Adsorbent Dose

Effect of adsorbent dose on removal of phenol was studied by varying the dose of adsorbent (0.01, 0.02, 0.05, 0.1, 0.15, and 0.2 g) in 100-mL unbuffered aqueous phenol solution while initial concentration of phenol was maintained at 250 mg/L. Results are shown in Fig 3.

Figure 3 shows that, at a dosage level below 0.1 g, phenol removal increased significantly as the adsorbent dose increased. Increase in percentage removal of phenol was caused by the availability of a larger surface area with more active functional groups (Mohanty et al 2005). When the adsorbent dose increased from 0.1 to



Figure 2.   Effect of pH on adsorption of phenol (carbon dosage = 0.1 g; phenol concentration = 250 mg/L; equilibration time = 100 min).
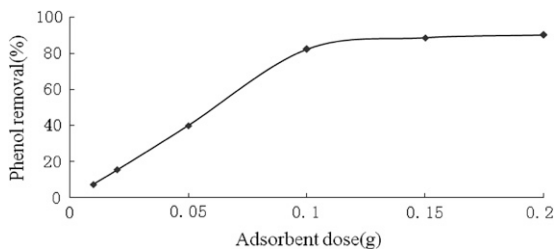


Figure 3.   Effect of adsorbent dose on adsorption of phenol (phenol concentration = 250 mg/L; equilibration time = 100 min).

0.2 g, no further increase in phenol removal was observed. Therefore, the optimum adsorbent dose was 0.1 g.

Similar phenomena were also observed by other researchers. Rengaraj et al (2002) reported that the optimum adsorbent dosage was approximately 0.1 g. Satendra et al (1987) found that removal of phenols can be affected by the level of adsorbent used.

**Effect of Temperature**

Effect of temperature on phenol removal was studied at a temperature range 20-45°C. Results are shown in Fig 4.

As temperature increased from 20 to 25°C, phenol removal slowly increased, and as temperature further increased from 25 to 30°C, phenol removal increased from 81.92 to 83.21%. As temperature increased beyond 30°C, phenol removal decreased sharply. Results indicate that maximum adsorption for phenol was obtained at 30°C for activated carbon prepared from WFB.

Similar trends were found in research of adsorption of phenol from aqueous solution on activated carbon at 278, 298, and 323 K (Ravi et al 1998).

**Adsorption Kinetic Studies**

Rate constant of adsorption was studied under the pseudo-first-order equation and the pseudo-second-order equation.
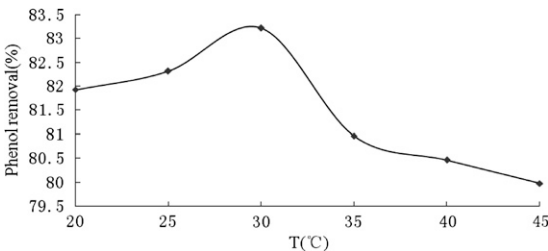


Figure 4.   Effect of temperature on adsorption of phenol (carbon dosage = 0.1 g; phenol concentration = 250 mg/L; equilibration time = 100 min).

The pseudo-first-order equation is represented by the following equation:

$$\ln(q_e - q) = \ln q_e - k_l \times t \qquad (2)$$

where q (mg/g) is the amount of phenol sorbed at time t (min), $q_e$ (mg/g) is the amount of phenol sorbed at equilibrium, and $k_l$ (1/min) is the first-order adsorption rate constant. The linear plot of ln ($q_e$-q) vs t is shown in Fig 5.

The pseudo-second-order equation (Ho and McKay 1999) based on equilibrium adsorption is expressed as

$$t/q = 1/\left(k_2 \times q_e^{\,2}\right) + t/q_e \qquad (3)$$

where $k_2$ (g mg min$^{-1}$) is the rate constant of second-order adsorption. Also, the linear plot is shown in Fig 6.

Constants and $R^2$ values obtained from the two linear plots are summarized in Table 2. The correlation coefficients, $R^2$, showed that the pseudo-second-order equation was more suitable for the experimental data. The data show that good
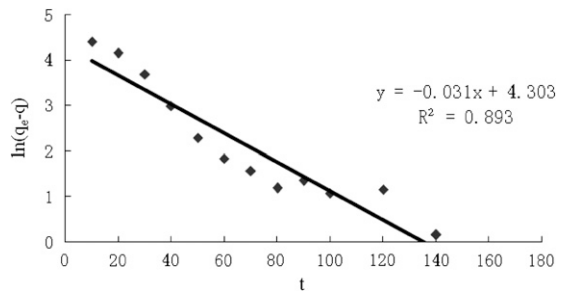


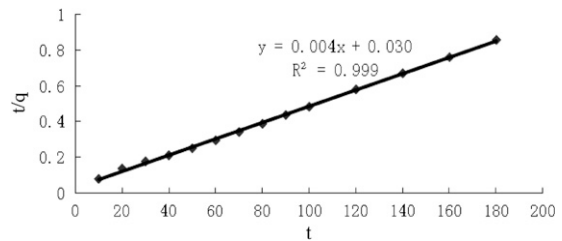Figure 5.   First-order adsorption rate of phenol on activated carbon.



Figure 6.   Second-order adsorption rate of phenol on activated carbon.

Table 2. Parameters of different adsorption rate of phenol on activated carbon.

| Pseudo-first-order equation | | | Pseudo-second-order equation | | |
|---|---|---|---|---|---|
| $q_e$ (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg/g) | $k_2$ (g mg min$^{-1}$) | $R^2$ |
| 209.558 | 0.0319 | 0.8933 | 217.39 | 0.0007 | 0.9991 |

agreement between the experimental and calculated $q_e$ values was observed by using the pseudo-second-order equation. As a result, it is concluded that adsorption of phenol on the activated carbon prepared from WFB follows the pseudo-second-order model. As expected, the overall rate of the adsorption process was controlled by chemisorption (Ho and McKay 1999).

## Adsorption Isotherms

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

Langmuir adsorption isotherm was given by the following equation (Langmuir 1918).

$$C_e/q_e = 1/(q_m \times b) + (1/q_m) \times C_e \qquad (4)$$

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. Linear plots of $C_e/q_e$ vs $C_e$ are shown in Fig 7.

The Freundlich adsorption isotherm was given by the following equation (Freundlich 1906):

$$q_e = K_f C_e^{1/n} \qquad (5)$$

where $K_f$ and n are Freundlich constants related to adsorption capacity and adsorption intensity. Usually, for a good adsorbent, $1 < n < 10$. The
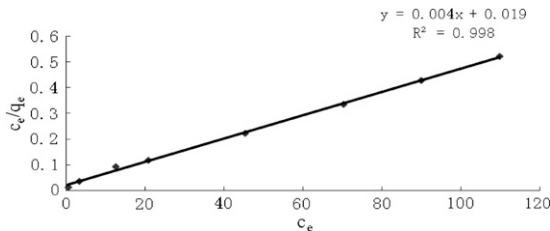


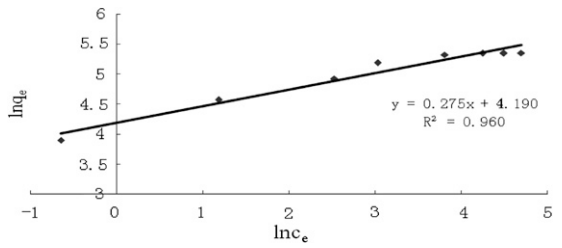Figure 7. Linear plot from Langmuir equation of phenol adsorption on activated carbon.



Figure 8. Linear plot from Freundlich equation of phenol adsorption on activated carbon.

Table 3. Parameters of different isotherms of adsorption of phenol on activated carbon.

| Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|
| $q_m$ (mg/g) | B | $R^2$ | n | $K_f$ | $R^2$ |
| 217.39 | 0.2408 | 0.9985 | 3.637 | 66.069 | 0.9604 |

phenol adsorption isotherm followed the linearized Freundich model (Fig 8).

Values of the Langmuir and Freundlich constants obtained are given in Table 3. It can be seen that the Langmuir model fit the results better than the Freundlich model. Because the value of 1/n was less than 1, it indicated a favorable adsorption. Similar trends were found in Fierro et al (2008), in which the Langmuir fit better in adsorption of phenol.

### CONCLUSION

The study results indicated that nitrogen-enriched activated carbon made from WFB had significantly higher phenol adsorption capacity compared with other nonnitrogen-containing activated carbon. The kinetics of phenol adsorption rate followed the pseudo-second-order equation, and the Langmuir model fit better than the Freundlich model in phenol adsorption in the study of adsorption isotherm.

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