Study on Adsorption Properties of Modified Activated Carbon Fiber

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Abstract. In this paper, the adsorption behavior of nitrobenzene from wastewater on modified activated carbon fiber was studied. The results showed that HNO₃ modified activated carbon fiber had the best adsorption performance. The optimum adsorption conditions were absorbent dosage 0.8g/50mL, the equilibrium time 60 minutes, and the removal of nitrobenzene increased with increasing the temperature of the system. The kinetics of adsorption indicated that the adsorption followed second-order kinetic equation.

1. Introduction
With the rapid development of industry and agriculture, nitrobenzene is widely used in the field of dyes, spices, explosives and other organic synthesis industries. A large amount of nitrobenzene wastewater is discharged during the production, storage, transportation and destruction. The nitrobenzene wastewater is carcinogenic, teratogenic and mutagenic. The serious environmental problems will be brought if improper treatment.

In recent years, many adsorption materials such as active carbon, biochar and kinds of peels [1] have been used as adsorbent to removal kinds of hazardous materials from waste water effectively [2, 3].

Modified activated carbon fiber (MACF) was used as adsorbent for removal of nitrobenzene from the waste water in this study. The effect of adsorbent dosage, the adsorption equilibrium time, temperature and kinetics of adsorption are discussed.

2. Experimental and methods

2.1. Materials
The activated carbon fiber (ACF) used in the present work was obtained from Shanghai, China. Wastewater was obtained from a factory (Yingkou, China). All reagents were used in the experiments from Tianjin Da Mao Reagent Co., Ltd.

2.2. Modification Experiments
The activated carbon fiber was soaked in distilled water for 5 hours to remove surface impurities and dried up. The modification methods for activated carbon fiber were as follows: The activated carbon fiber was impregnated in ethanol solution according to the impregnation ratio of 1:3, 0.1mol/L HNO₃,
0.1mol/L HCl, 0.1mol/L NaOH, and 0.5% CuSO₄ solution for 12h and dried at 105 °C. After impregnation, the activated carbon fibers were washed with distilled water until the solution was neutral and dried at 105 °C for later experiment. The 0.5 grams ACF modified by different methods was put into 50mL wastewater in cone-shaped bottle to adsorb 180 min at 25 °C in the modification adsorption experiment.

2.3. Adsorption Experiment
A certain amount of activated carbon fiber and 50mL wastewater were added to 100mL cone-shaped bottle. The solution was vibrated in oscillator at different temperatures. The wastewater was filtered after shaking a period of time and removal recent of nitrobenzene was determined by COD of wastewater. COD of the filter was tested by a DR 2800 spectrophotometer (HACH, USA).

The influence factors of contact time, adsorbent dosage and the temperature were studied. The temperatures were set at (20, 30, 40 and 50 ± 0.2 °C) for wastewater in this influence factor.

The COD adsorption at equilibrium, \( q_e , \text{mg/g} \), at any time \( q_t, \text{mg/g} \) and COD removal (%) was calculated as follows:

\[
q_e = \frac{(\text{COD}_0 - \text{COD}_e)V}{W} \tag{1}
\]

\[
q_t = \frac{(\text{COD}_0 - \text{COD}_t)V}{W} \tag{2}
\]

\[
\text{COD Removal} (%) = \frac{(\text{COD}_0 - \text{COD}_e)}{\text{COD}_0} \times 100 \tag{3}
\]

Where \( \text{COD}_0 \) (mg/L) is the initial COD of wastewater, \( \text{COD}_e \) is the equilibrium COD of wastewater and \( \text{COD}_t \) is the wastewater COD at any time, respectively, \( V \) (L) is the volume of wastewater, and \( W \) (g) is the adsorbent weight.

3. Results and Discussions

3.1. Effects of Modification Method on Adsorption
The effects of modification method of ACF on adsorption were shown in Fig.1. The results can be seen that the adsorption performance of modified ACF was better than unmodified. Especially, the ACF modified by 0.1mol/L HNO₃ solution had the best adsorption performance on nitrobenzene, and the removal rate of COD reached 50 %, which was nearly twice as high as that of unmodified ACF.

![Figure 1. Effects of Modification Method.](image-url)
3.2. *Effects of Adsorption Time*

Adsorption equilibrium time is an important factor in adsorption study. Fig. 2 indicated that the effect of adsorption time on nitrobenzene from wastewater for ACF modified by HNO$_3$. As shown in Figure 2, the removal rate of COD increased rapidly in 0 ~ 30 min, and remained almost constant after 60 min, that was, the adsorption equilibrium time was 60 min. It can be also seen that the adsorption time was relatively short, which may be related to the pore structure of ACF. The pore was advantageous to the diffusion between adsorbent and adsorbent, which reduced the adsorption time.

![Figure 2](image_url)

*Figure 2. Effects of Adsorption Time.*

3.3. *Effects of Temperature*

Fig. 3 shows the effect of adsorption temperature (20°C, 30°C, 40°C, 50°C) on the adsorption of nitrobenzene. It can be seen from Fig. 3 that the removal rate of COD increased with the increase of temperature. The results showed that the process of MACF adsorbing nitrobenzene was endothermic reaction, and increasing temperature was advantageous to the adsorption of nitrobenzene. This is mainly due to that raising the temperature, the speed of solute molecule migration accelerated and the viscosity of the solution decreased, which was benefit to the adsorption of solute molecules.

![Figure 3](image_url)

*Figure 3. Effects of Adsorption Temperature.*
3.4. Kinetic Analysis

The kinetic analysis of adsorption nitrobenzene on MACF was studied by Lagergren’s pseudo-first-order model, Pseudo second-order model and intraparticle diffusion model [4].

Lagergren’s pseudo-first-order is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{q_e} t$$

The pseudo second-order equation is expressed as [5]:

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

The intraparticle diffusion equation can be presented as follows [6]:

$$q_i = k_{ip1} t^{1/2} + c_i$$

Where $q_e$ and $q_t$ (mg/g) are the amounts of COD adsorbed (mg/g) at equilibrium and any time t (min), respectively and $k_1$ (1/min) is the rate constant for pseudo-first-order adsorption. $k_2$ (g/mg min) is the pseudo second-order constant, $k_{ip1}$ (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant at stage $i$, and $c_i$ is the intercept at stage $i$. Table 1 lists three models parameters of nitrobenzene adsorption by MACF at different temperatures. The higher correlation coefficient value ($R^2 > 0.99$) listed in Table 1 indicates that nitrobenzene adsorbed on MACF follows pseudo second-order model. The intraparticle diffusion model gives the mechanism of adsorption and rate-controlling steps of adsorption. The value of $k_{ip1}$ is larger than $k_{ip2}$, and $c_2$ is larger than $c_1$ in the condition of all the temperatures. This indicates that the adsorption efficiency is higher in the beginning due to the large number of vacant sites on MACF surface. After the adsorbed materials form a thick layer, the capacity is exhausted and the adsorption efficiency is controlled by the rate at which the adsorbent is transported from the exterior to the interior sites of the adsorbent.

| Kinetic model       | Parameter                  | 20°C       | 30°C       | 40°C       | 50°C       |
|---------------------|----------------------------|------------|------------|------------|------------|
| pseudo-first-order  | $q_e$(cal) (mg/g)          | 2.6714     | 2.6807     | 2.6442     | 2.7011     |
|                     | $k_1$(min$^{-1}$)          | 0.00921    | 0.00401    | 0.00512    | 0.01126    |
|                     | $R^2$                      | 0.8498     | 0.8281     | 0.7784     | 0.9025     |
| pseudo second-order | $q_e$(cal)(mg/g)           | 9.33       | 9.52       | 9.67       | 9.88       |
|                     | $k_2$(min$^{-3}$)          | 0.04145    | 0.03821    | 0.03802    | 0.03524    |
|                     | $R^2$                      | 0.9998     | 0.9998     | 0.9999     | 0.9999     |
| intraparticle       | $K_{ip1}$(mg/g min$^{0.5}$)| 0.11431    | 0.15288    | 0.16332    | 0.17477    |
| diffusion           | $C_1$                      | 5.53405    | 4.80433    | 4.90765    | 4.92579    |
|                     | $R^2$                      | 0.9666     | 0.9744     | 0.9658     | 0.9742     |
|                     | $K_{ip2}$(mg/g min$^{0.5}$)| 0.01409    | 0.01376    | 0.01025    | 0.01259    |
|                     | $C_2$                      | 5.13232    | 4.98546    | 5.03584    | 5.53098    |
|                     | $R^2$                      | 0.9873     | 0.9044     | 0.8965     | 0.8986     |
| $q_e$(exp)(mg/g)     | 9.33                       | 9.52       | 9.67       | 9.88       |

4. Conclusion

HNO$_3$ Modified activated carbon fiber is a better material for removal nitrobenzene from wastewater. The better adsorption behaviors are absorbent dosage 0.8g/50mL and adsorption time 60 minutes. The thermodynamics studies suggest that the process of nitrobenzene removed from wastewater is an
endothermic process. Adsorption of nitrobenzene follows the pseudo second-order kinetics well. Intraparticle diffusion is responsible for adsorption but it is not the only rate-controlling step.

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