

Adsorption and photocatalytic degradation of phenol over TiO₂/ACF^①

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Abstract: The adsorption and photocatalytic degradation of phenol in water were investigated in a cylindrical borosilicon glass photoreactor with a cooling water jacket using TiO₂/ACF as photocatalyst. A 15 W UV lamp (254 nm) was used as central light source. The effects of the temperature and initial concentration of phenol solution on adsorption and photocatalytic process were studied, and the comparison of adsorption, photolysis and photocatalysis was conducted. The results show that the classical model of Langmuir gives a good description of the adsorption of phenol on TiO₂/ACF and low temperature can improve the adsorption of phenol on photocatalyst; increasing temperature can increase the photocatalytic degradation rate of phenol; and the adsorption enhances the photocatalytic removal of phenol.

Key words: phenol; titanium dioxide; activated carbon fiber; adsorption; photocatalysis

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1 INTRODUCTION

Today, water pollution caused by hazardous organic chemicals used in industry and agriculture is a very serious problem, the deep treatment and reuse of wastewater is very indispensable^[1]. Titanium dioxide heterogeneous photocatalysis can degrade most of organic pollutants completely into CO₂, H₂O and inorganic acid, and has shown tremendous potentiality in the treatment of wastewater^[2]. TiO₂ powder has been the most widely used photocatalyst in the photocatalytic process due to its stable chemical properties, easy access and cheap cost. However, this method has several drawbacks and the following two, in particular, limit its widespread applications: 1) during extended use, the catalyst has a tendency to coagulate with a corresponding decrease in its activity and the difficulty of separating from aqueous phase; 2) reaction rates are limited by slow electron transfer from the catalyst to dioxygen^[3]. So to overcome the problems of powder separation and low light quantum yield, studies to immobilize the TiO₂ and improve the efficiency of photocatalysis have been undertaken and a variety of substrates have been considered, including glass, alumina, titanium mesh, glass fiber^[4-7]. With the development of fiber industry, activated

carbon fiber (ACF) emerged to be a novel kind of functional material. Because of its big surface area and strong adsorption capacity, ACF has been used as new substrate and adsorbent. In recent studies, we also found that the adsorption of organic pollutant onto TiO₂ particles could strikingly enhance the photocatalytic rate^[8-11]. Hence, in this paper activated carbon fiber was employed as substrate to support TiO₂ which is immobilized by coating technique, and phenol was used as a pollutant for photocatalysis study under UV irradiation. The objective of this research is to make use of ACF's high adsorption activity for organic substances which can enable the pollutants to be concentrated on the surface of loaded TiO₂, and tries to improve the degradation rate of photocatalytic process using immobilized TiO₂ as photocatalyst.

2 EXPERIMENTAL

2.1 Reagents and instruments

Commercial TiO₂ powder purchased from German was anatase by X-ray diffraction and activated carbon fiber with a specific surface area of 697.3 m²/g was made in Institute of Coal Chemistry, Chinese Academy of Sciences. Distilled water was used

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throughout the test. Other chemicals were obtained as analytical grade reagents and used without further purification. A 15 W lamp with a maximum UV irradiation peak at 254 nm was used as central light source and a spectrophotometer (721 Shanghai Third Analytic Instrument Plant) was used for detecting the concentration of phenol in solution.

2.2 Preparation of TiO₂/ACF photocatalyst

Prior to using the new purchased ACF was thoroughly cleaned with distilled water to remove the possible trace organic substances and dried in the air. In the presence of dispersant, a solution with quantitative TiO₂ was stirred for 4 h and shaken in an ultrasonic cleaner (KQ5200, Kunshan Ultrasonic Instrument Limited Corporation) for 24 h, then a uniform TiO₂ solution was made. The TiO₂ suspension was coated on ACF substrate, and the supported TiO₂ was gradually heated to 180 °C and maintained for 2 h, then cooled to room temperature. The whole process of coating was repeated again for two times and then TiO₂/ACF photocatalyst was obtained. The crystalline pattern of immobilized TiO₂ was still anatase.

2.3 Experimental procedure

2.3.1 Adsorption equilibrium experiments

The experiment of adsorption isotherm of phenol on TiO₂/ACF was conducted in static state at 25 °C. A series of weighed TiO₂/ACF was placed in the 50 mL of phenol solutions with various initial concentrations at natural pH (about 7). After the solutions were stirred for 48 h, the concentrations of phenol were determined by 4-aminantipyrine method using 721-spectrophotometer under 510 nm. The amount of equilibrium adsorption q_e was determined from the material balance $q_e = V(c_0 - c_e)/m_A$, where V is the volume of phenol solution (L); c_0 is the initial concentration of phenol solution (mg/L); c_e is the equilibrium

concentration of phenol solution (mg/L); m_A is the mass of adsorbent in grams (since the adsorption was the corporate contribution of TiO₂ and ACF, the mass of adsorbent in the experiments was the sum of the two substances).

2.3.2 Kinetic experiments

Adsorption, photolysis and photocatalysis kinetic experiments were carried out in a cylindrical borosilicon glass photoreactor with a cooling water jacket to maintain the reaction temperature. Air was bubbled into reactor uniformly at a speed of 60 mL/s to supply oxygen and reduce the effect of material transfer. Adsorption kinetic experiments were carried out under no light source. Water samples were collected from the reactor at designated time intervals during reaction to determine the concentrations of phenol by 4-aminantipyrine method using 721-spectrophotometer under 510 nm.

3 RESULTS AND DISCUSSION

3.1 Adsorption isotherm of phenol

Many researchers^[4, 12] have applied the Langmuir expression to analyze the adsorption behavior of organics in heterogeneous adsorption process and have also successfully applied to heterogeneous photocatalytic process. In order to evaluate the properties of TiO₂/ACF adsorbent, this test was designed to study the adsorption isotherm of phenol, and the relation between equilibrium amount of adsorption and equilibrium concentration of phenol is shown in Fig. 1 (a), the relation of c_e/q_e versus c_e is shown in Fig. 1 (b).

The result in Fig. 1(b) indicates that the adsorption of phenol on TiO₂/ACF follows the Langmuir adsorption model:

$$q_e = q_m K c_e / (1 + K c_e) \quad (1)$$

where K is the adsorption equilibrium constant, q_e is the equilibrium amount of adsorption on the

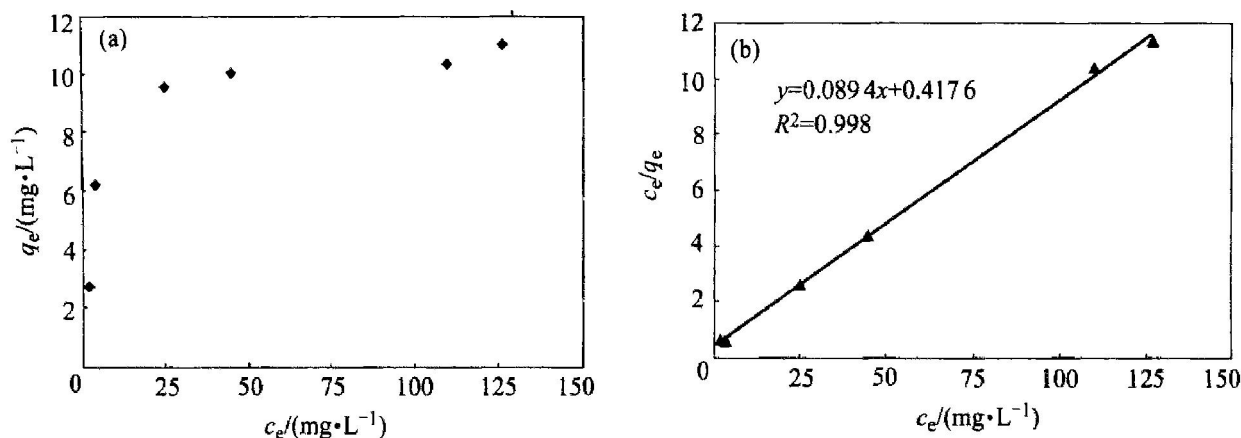


Fig. 1 Adsorption isotherms of phenol
($\theta = 25$ °C, $V = 50$ mL, pH = 7)

TiO_2/ACF ; q_m is the maximum adsorbed amount and c_e is the equilibrium concentration in solution. Then the parameters of Langmuir model for phenol adsorbed on TiO_2/ACF can be calculated from the straight line, and the results are: $q_m = 11.1857 \text{ mg/g}$, $K = 0.2141 \text{ L/mg}$.

3.2 Comparison of photolysis, photocatalysis and adsorption of phenol

It is well known that the first step of organic oxidative decomposition is oxidation reaction of the organic molecules with hydroxyl radicals produced on the photocatalyst surface. Adsorption process of organic pollutant on photocatalyst is very important for the heterogeneous photocatalytic reactions^[13]. In order to reveal some valuable information leading to a better understanding of the photocatalytic performance, Fig. 2 gives the comparative results of the changes of phenol remaining with reactive time in adsorption, photolysis and photocatalysis process, respectively. In adsorption process the results show that 75% of phenol was adsorbed on TiO_2/ACF under 3.0 h adsorption in a dark condition without UV irradiation, which means that the TiO_2/ACF has obvious adsorption for phenol in aqueous solution. In photolysis process the disappearance of phenol reached 96% after 3.0 h reaction, which demonstrates that the short wavelength light (254 nm) has strong photodecomposition to phenol molecules owing to the direct contact of UV-lamp with phenol solution and the phenol molecules do absorb this UV light. In photocatalytic process, the removal rate of phenol only reached 97.14% at the end of reaction, but it should be noticed that the degradation rate of photocatalysis seems to be apparently higher than that of photolysis within the first one hour, which means that the combined efforts of UV and TiO_2/ACF achieved better performance. The reason is that UV irradiation induces the formation of electrons (e^-) and holes (h^+) on the semiconductor surface. The photogenerated holes (h^+) react with the adsorbed OH^- and high activity $\cdot\text{OH}$ radicals are produced. The $\cdot\text{OH}$ radicals can react with any substances non-selectively. The photogenerated holes (h^+) can also deprive the electrons of organic pollutant directly and oxidize it into radicals. Meanwhile, dissolved oxygen (DO) in water can capture electron and produce O_2^- which react with phenol or phenolic intermediates. Moreover, DO can further form into $\cdot\text{OH}$ under protonation resulting^[14] in degradation of phenol. The test of phenol volatility was also done under this experimental condition but without TiO_2/ACF and in the dark, the results showed that there was almost no change in the concentration of phenol during test time.

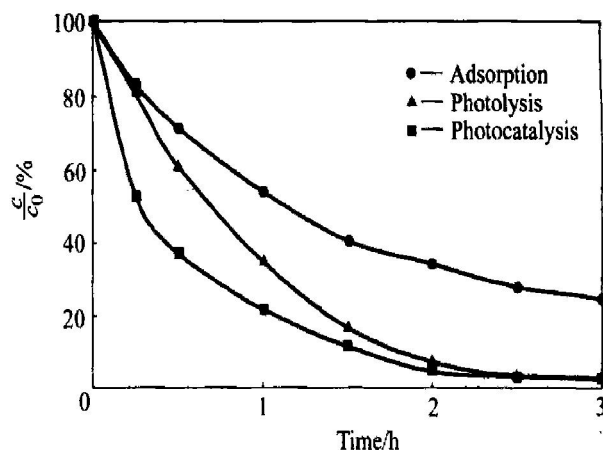


Fig. 2 Adsorption, photolysis and photocatalysis of phenol

Experimental conditions: $c_0 = 100 \text{ mg/L}$, $\text{pH} = 7$, $V = 100 \text{ mL}$, $m(\text{TiO}_2/\text{ACF}) = 2.11 \text{ g}$, $\theta = 25^\circ\text{C}$

3.3 Effects of temperature on adsorption and photocatalysis

Temperature is an important factor affecting the adsorption and photocatalysis, this test was conducted under two different temperature of 25°C and 35°C . The results are shown in Fig. 3.

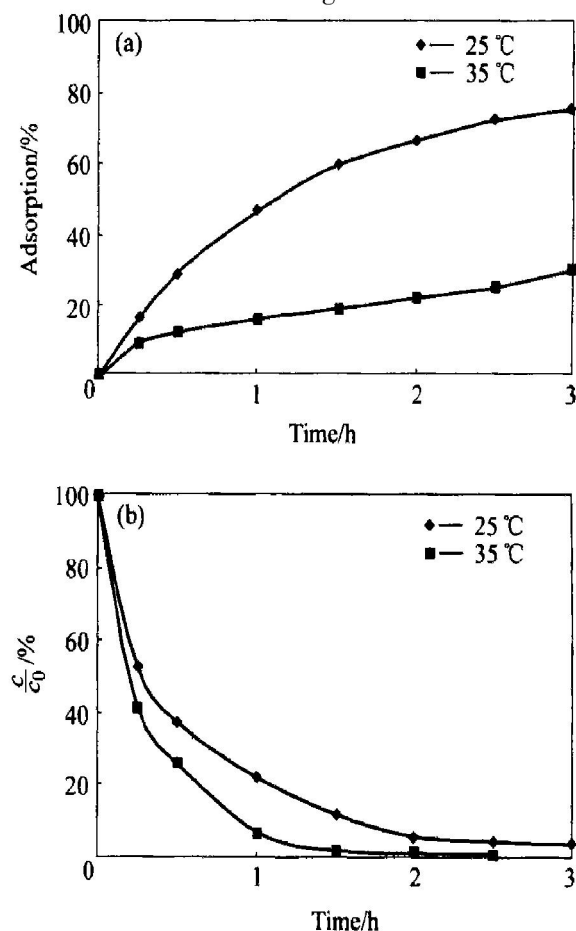


Fig. 3 Effect of temperature on adsorption and photocatalysis

Experimental conditions: $c_0 = 100 \text{ mg/L}$, $\text{pH} = 7$, $V = 100 \text{ mL}$, $m(\text{TiO}_2/\text{ACF}) = 2.11 \text{ g}$

Fig. 3(a) shows that the temperature has a great influence on the phenol adsorption at TiO₂/ACF. Under experimental conditions the adsorption rate decreases with increasing temperature because the adsorption is a heat releasing process, then low temperature favors the adsorption of phenol at TiO₂/ACF. In the case of photocatalytic process as shown in Fig. 3(b), the photocatalytic degradation rate increases with increasing temperature. At 25 °C the phenol removal rate is 97.14% after 3 h reaction, while at 35 °C the phenol disappears fast, especially during the first 1 h, only 1.5 h irradiation the phenol removal almost achieves 100%. The results indicate that the reaction rate plays a more important role than adsorption rate in the degradation process of phenol.

3.4 Effects of initial concentration on adsorption and photocatalysis

To study the influence of the initial phenol concentration on adsorption and photocatalysis, a set of tests were performed. In these studies, only the initial concentration of phenol was changed while the other experimental conditions were kept constant. The variation of adsorption rate against time is depicted in Fig. 4. From Fig. 4 we can see that the adsorption rate of phenol on TiO₂/ACF increases with increasing initial concentration.

The effect of initial concentration on photocatalysis is shown in Fig. 5(a). Data showing a straight line of $-\ln c/C_0$ versus time corresponding with Fig. 5(a) is plotted in Fig. 5(b). The results of test indicate that in our experimental conditions the photocatalytic reaction follows apparent first-order reaction kinetics, which is in agreement with reports in Refs. [15–17] that photocatalytic degradation of organic pollutant in the low concentration obeys pseudo-order reaction equation. The equation is given as follows:

$$-dc/dt = kc \quad (2)$$

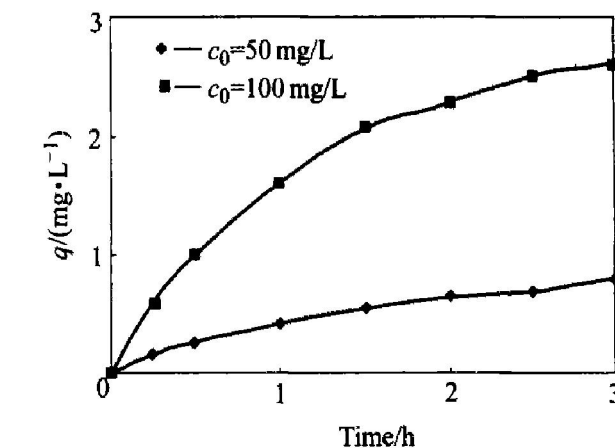
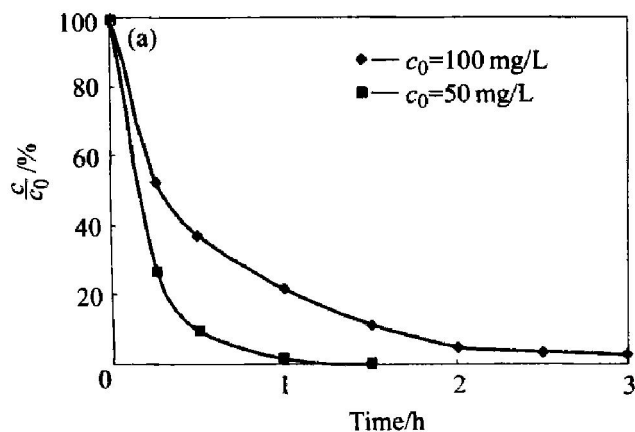


Fig. 4 Effect of initial concentration on adsorption

Experimental conditions: $V = 100$ mL, $t = 25$ °C, $\text{pH} = 7$, $m(\text{TiO}_2/\text{ACF}) = 2.11$ g

where k represents rate constant and c is the concentration of solute. The value of k can be determined from the slope of the straight line ($c_0 = 50$ mg/L, $k = 6.69 \times 10^{-2} \text{ min}^{-1}$; and $c_0 = 100$ mg·L⁻¹, $k = 2.01 \times 10^{-2} \text{ min}^{-1}$). As shown in Fig. 5, in the region of our studies, the apparent first-order rate constant decreases with increasing initial concentration while the reaction rate and the amount of phenol adsorbed on TiO₂/ACF increase with increasing initial concentration.

4 CONCLUSIONS

1) TiO₂/ACF can solve the problem of separating TiO₂ power from water, and has a cooperative effect in the photocatalytic process, thus it can be used in the deep treatment of wastewater.

2) The adsorption of phenol on TiO₂/ACF follows the Langmuir adsorption model; the photocatalytic degradation obeys the pseudo first-order kinetic equation.

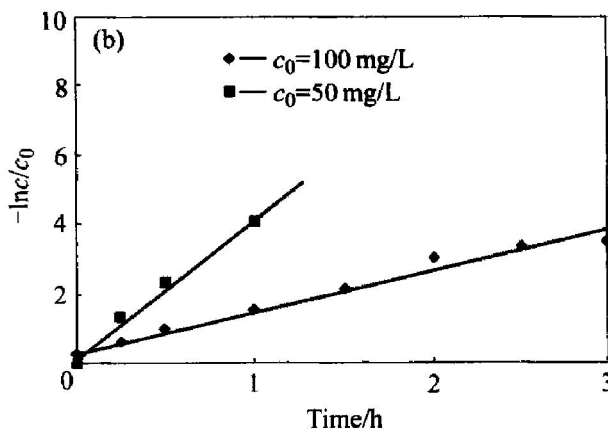


Fig. 5 Effect of initial concentrations on photocatalysis

Experimental conditions: $v = 100$ mL, $\theta = 25$ °C, $\text{pH} = 7$, $m(\text{TiO}_2/\text{ACF}) = 2.11$ g

3) The temperature and initial concentration of phenol have a great effect on adsorption and photocatalysis. With increasing temperature the rate of adsorption decreases while the photocatalytic degradation increases, which means that the decrease of activation energy plays an important role; the high initial concentration can improve adsorption and photocatalysis.

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