Effect of Lamp Power and Its Position on Photocatalytic Degradation of Phenol in Aqueous Suspension of TiO$_2$

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The photocatalytic degradation of phenol under irradiation with UV light was investigated in aqueous suspension of nano titanium dioxide (TiO$_2$). The effects of photocatalyst such as TiO$_2$ (anatase) and TiO$_2$-P25 and power of UV-lamp along with position on the photocatalytic degradation of phenol have been studied. The degradation kinetics was analyzed by the change in phenol absorbance employing UV-vis spectrometry as a function of irradiation time. The degradation follows first order kinetics. TiO$_2$-P25 was found to be more reactive than TiO$_2$ (anatase) which is attributed to small crystalline size. Horizontal position of the lamp was found to be better than vertical position of lamp. The degradation was also enhanced with increased in power of UV lamp.

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Keywords: Phenol; Catalysis; Degradation; Titanium dioxide; UV lamp

I. INTRODUCTION

The presence of organic pollutants in aquatic environment has caused several environmental problems since couple of decades. Phenol and phenolic compounds are major pollutants of aquatic environment. Phenol may occur in the aquatic environment due to its widespread use in agricultural, petrochemical, textile, paint, plastic and pesticidal chemical industries. Phenol cause serious environmental problems because of toxicity, strong odor emission, carcinogenic and mutagenic potential to mammalian and aquatic life [1]. The increase discharge of this emission, carcinogenic and mutagenic potential to mammalian and aquatic life [1]. The increase discharge of this emission, carcinogenic and mutagenic potential to mammalian and aquatic life [1]. The increase discharge of this emission, carcinogenic and mutagenic potential to mammalian and aquatic life [1]. The increase discharge of this emission, carcinogenic and mutagenic potential to mammalian and aquatic life [1]. 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Advanced oxidation processes (AOPs) including heterogeneous photocatalysis is a promising methods for water treatment. AOPs are based on the generation of the strongly oxidizing hydroxyl radicals (•OH), which oxidize a broad range of organic pollutants present in water and wastewaters [2, 4, 5]. Many semiconductors have photocatalytic properties [6–8], the nano titanium dioxide (TiO$_2$) appears the most efficient and popular photocatalyst [9] because of its outstanding photocatalytic activity, inertness [10], its stability within a wide range of pH [7], and inexpensive photosensitized material [11].

The band gap of TiO$_2$ is 3.2 eV and an efficient photoreactivation process begins when the TiO$_2$ particle absorbs light at a wavelength smaller than 387 nm. The valence band electron promotes through the bandgap to the conduction band ($e_{\text{CB}}$), leaving a valence band hole ($h_{\text{VB}}$) behind, generating an electron-hole ($e_{\text{CB}}$-•$h_{\text{VB}}$) pair. The generated electron-hole pairs must be trapped in order to avoid recombination [12]. These pairs are able to initiate oxidation and reduction reactions on the TiO$_2$ surface. The $h_{\text{VB}}$ can oxidize the organic molecules sorbed on the surface either directly or indirectly, through the formation of •$\text{OH}$ radicals. On the other hand, oxygen over the TiO$_2$ surface traps the $e_{\text{CB}}$, produce the superoxide radical anion (O$_2$•$^-$) which is unstable, reactive and involves into more •$\text{OH}$. The whole mechanism is given by the following Eqs. (1)-(5):

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow \text{TiO}_2 + e_{\text{CB}} + h_{\text{VB}} \quad (1) \\
h_{\text{VB}} + \text{OH}^- & \rightarrow \bullet \text{OH} \quad (2) \\
h_{\text{VB}} + \text{H}_2\text{O} & \rightarrow \bullet \text{OH} + \text{H}^+ \quad (3) \\
e_{\text{CB}} + \text{O}_2 & \rightarrow \text{O}_2^- \quad (4) \\
2\text{O}_2^- + 2\text{H}_2\text{O} & \rightarrow 2\bullet \text{OH} + 2\text{OH}^- + \text{O}_2 \quad (5)
\end{align*}
\]

Previously, we have reported the photocatalytic degradation of phenol under the influence of various operational parameters [13]. In the present work, the model pollutant of water chosen for photocatalytic degradation study was phenol. The effects of photocatalysts and the power of UV-lamp on the photocatalytic degradation of phenol were examined in term of kinetics. UV-vis spectroscopy is employed to attempt to rationalize result of photocatalytic degradation studies.

II. EXPERIMENT

A. Materials

Photocatalyst TiO$_2$ (anatase, particle size ≤ 30 nm) obtained from Jiangsu Hehui Nanometer Science and Technology Co., Ltd. (China) was used in most of the experiments. TiO$_2$-P25 (composed of ca. 80% anatase and 20% rutile; particle size 21 nm) product of Degussa Co., Germany was used for comparative studies. Analytical reagent grade phenol and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as such without further purification. De-ionized distilled water used for all aqueous preparations and was obtained from a Milli-Q Gradient A-10 system (Millipore).

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Photocatalytic degradation experiments were performed with an open Pyrex-glass cell with 500 mL capacity. The photocatalytic degradation set up is shown in Fig. 1. During the dark experiment and irradiation, the beaker was wrapped with aluminum foil to shield it from the ambient light and to increase reflection. An aqueous suspension was prepared by the nano TiO$_2$ (200mg/L) with an aqueous solution of phenol (3.56x10$^{-4}$ M, 200 mL). Before irradiation, the suspensions were placed on a magnetic stirring plate in a flow of oxygen for ca. 15 min under the dark to ensure the equilibrium of the solution. The irradiation was carried out using 15 W UV-lamp (Ya Ming Co., Shanghai, China) and 125 W lamp (Leijian Special Light Source Ltd. Co., Shenzhen, China), emitting mainly at 365 nm wavelength. Distance between the lamp and solution surface was 12 cm. The pH of solutions was measured using 8682 digital pH meter (AZ Instrument Corp., Taiwan) by adding HCl (0.1M). All experiments were conducted at 298±1 K.

C. Analysis

At any given irradiation time interval, aliquots of 7 mL of the solution were withdrawn. The liquid samples were centrifuged at 3000 rpm for 10 min and subsequently filtered to separate nano TiO$_2$ particles. The filtered samples were stored at 4°C prior to analysis. The quantitative determination of phenol in the filtrates was performed by measuring its absorption at 270 nm through the UV-vis spectrophotometer (Helios Gamma Thermo Spectronic, Cambridge, England). A quartz cell with a path length of 1 cm was used for spectrophotometric measurements. The degree of photocatalytic degradation ($X$) of each sample was calculated from the equation given below:

$$X = \frac{A_0 - A_t}{A_0},$$

where $A_0$ is the absorbance at zero time and $A_t$ is the absorbance at time $t$.

III. RESULTS AND DISCUSSION

Photocatalytic degradation of phenol in aqueous suspension of nano TiO$_2$ (anatase) was carried out. Different reactor designs are documented that can be used for photocatalytic degradation reactions [14, 15]. In this work, a simple photocatalytic degradation setup is used as shown in Fig. 1. Figure 2 shows the degree of degradation as a function of irradiation time of aqueous solution of phenol. It can be seen from Fig. 2 that in the presence of TiO$_2$/UV light, 68.4% of phenol was degraded after 10 h irradiation. While only 6.5% of phenol was degraded in the absence of TiO$_2$ under the same experimental conditions. It can be inferred from Fig. 2 that both UV light and catalyst (TiO$_2$) were required for efficient degradation of phenol suggesting that the phenomenon is initiated by photoexcitation of catalyst as described in Eqs. (1)-(5). Furthermore, control experiment showed that no significant direct photolysis was observed when the aqueous solution of phenol was irradiated without catalyst. The appropriate alignment of the lamp is important to obtain best results. Therefore, the position of the lamp which was significant for the degradation has been studied. Figure 3 shows the effect of lamp position on change in absorption intensity as a function of irradiation time of aqueous solution of phenol. It can be seen from Fig. 3 that horizontal position of the lamp facilitates the degradation phenomenon. The Langmuir-Hinshelwood kinetic equation has been observed to analyze the heterogeneous photocatalytic reaction by TiO$_2$ [16]. The photocatalytic reaction rate $r$ is given by:

$$\frac{dC_S}{dt} = -k_rKC_S,$$

where $r$ is the rate of reaction, $C_S$ is substrate (phenol) concentration, $t$ is time of the reaction, $k_r$ is the reaction rate constant and $K$ is adsorption constants associated.
and negatively charged in alkaline medium (pH > 6.8). Thus, the TiO$_2$ surface is positively charged in acidic medium (pH < 6.8) and negatively charged in alkaline medium (pH > 6.8). Acidic pH has been found to be favorable for the photocatalytic degradation of phenol molecules present in its anionic phenolate form. This is attributed to the fact that phenolate ion is negatively charged so an electrostatic attraction is developed, resulted in enhanced photocatalytic activity at pH ca. 5. Alternatively at pH 7 or above, presence of phenolate ion makes difficult the phenol molecule to approach the TiO$_2$ surface.

The power of the UV-lamp is a major factor, which can significantly influence the electron-hole pairs and in turn the production of photon and •OH, affecting photocatalytic degradation of phenol during photocatalytic process [18]. Two commercial UV lamps, 15 W and 125 W, were used to study the influence of different light source for comparison of photocatalytic degradation efficiency of phenol. An apparent decrease in the absorption intensity of phenol in aqueous solution was observed during irradiation with UV-lamp. Figure 5 shows the effect of UV-lamp power on the absorption intensity of phenol versus irradiation time. Experimental results indicate that the concentration of phenol decreased with increasing irradiation time and the apparent rate constant ($k_{app}$) for degradation of phenol increased with increasing power of UV-lamp. Table III shows the photocatalytic degradation was enhanced significantly with high power UV-lamp. The enhancement in $k_{app}$ with the increased power of UV-lamp (and thus its light intensity) is due to more number of electron-hole pair at the surface of TiO$_2$ catalyst [19]. This will be attributed to removal of phenol from the system. From Fig. 5, it can be concluded that high power UV-lamp enhances the possibility of light intensity contact between the phenol and photon. Thus higher power of lamp makes the degradation of phenol more significantly [19, 20].

In order to compare the photoactivity of catalysts, two different available TiO$_2$ catalyst, TiO$_2$ (anatase) and

| Lamp position | 15 W | 125 W |
|---------------|------|-------|
| $k_{app}$ (min$^{-1}$) | $R^2$ | $k_{app}$ (min$^{-1}$) | $R^2$ |
| Horizontal    | 0.0019 | 0.684 | 0.996 | 0.028 | 0.797 | 0.985 |
| Vertical      | 0.0016 | 0.596 | 0.989 | 0.017 | 0.646 | 0.990 |

Table I: Influence of the lamp position on kinetic results of phenol degradation.
The results are shown in Table III. Comparing the two types of titanium dioxide that were used, TiO$_2$-P25 catalyst was found to be more efficient for the photocatalytic degradation of phenol. The enhanced catalytic activity of TiO$_2$-P25 can be explained by the small nano-crystalline size than TiO$_2$ (anatase). The decrease in size provides a larger surface area to adsorb phenol and cause enhancement in photocatalytic degradation.

### IV. CONCLUSIONS

We examined the photocatalytic degradation of phenol as the model pollutant of water by TiO$_2$ (anatase) and TiO$_2$-P25 suspension in the presence of UV light. The degradation process follows first order kinetics. The photocatalytic degradation rate of phenol was found to be better for horizontal alignment of the lamp. Enhanced power of UV-lamp also influences the photocatalytic degradation significantly. Small nano-crystalline size of TiO$_2$-P25 exhibits better photocatalytic activity than TiO$_2$ (anatase) under similar conditions.

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**TABLE III: Effect of UV-lamp power on kinetic parameters of phenol photocatalytic degradation using two different TiO$_2$.**

| Catalyst       | Lamp power | $k_{app}$ (min$^{-1}$) | $X$ |
|----------------|------------|------------------------|-----|
| TiO$_2$ (anatase) | 15 W       | 0.0019                 | 0.684 |
|                | 125 W      | 0.0028                 | 0.797 |
| Enhanced factor | 15 W       | 0.0021                 | 0.711 |
| TiO$_2$-P25    | 15 W       | 0.0035                 | 0.858 |
|                | 125 W      | 0.0035                 | 0.858 |

*Enhancement factor*