

Preparation of TiO₂ nanoparticle and photocatalytic properties on the degradation of phenol

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Abstract. Titanium dioxide (TiO₂) nanoparticle in the diameter of 30-50nm in this study was prepared by sol-gel method. X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to investigate the characteristics of TiO₂ nanoparticle. The effect of amount of distilled water and absolute ethyl alcohol, calcination temperature on photocatalytic activity were explored on the degradation of phenol. The results showed that the optimal amount of distilled water and absolute ethyl alcohol and calcination temperature was 5mL, 90mL and 575°C, respectively. Moreover, in the photocatalytic activity test, the effect of TiO₂ nanoparticle amount and the pH value of phenol solution on the degradation of phenol were discussed. The results showed that the optimal amount of TiO₂ nanoparticle was 75mg in 150mL of phenol solution (100mg/L) and the degradation reached 92.4% when the pH value was 1. The utilization of TiO₂ nanoparticle on the degradation of phenol is promising for the coal-chemical wastewater.

1. Introduction

TiO₂ photocatalyst is suitable for coal-chemical wastewater due to its inexpensiveness, nontoxicity and high photochemical stability [1-4]. Generally, the photocatalysis is initiated when a photon excited by UV-light has equal or greater energy than its band gap, it would escape from valence band to conduction band and form electron (e⁻) and positive holes (h⁺). The generated positive holes (h⁺) and electrons (e⁻) transfer to different position on the photocatalyst surface and react with water into hydroxyl radicals(•OH) which have high oxidation activity and mineralize the organic contaminants into water and carbon dioxide [5-9]. In the recent years, many researches about TiO₂ have been reported. Antonopoulou et al. [10] prepared char/N-TiO₂ and char/N-F-TiO₂ composite photocatalysts to degrade the phenol (5mg/L) under solar light in 4 hours, although phenol was degraded all, the concentration of phenol was low. Zang et al [11] utilized TiO₂ to degrade phenol (20mg/L) in different pulsed discharge systems. TOC mineralization efficiency of phenol was enhanced to 65%, however, the concentration of phenol was low and the energy consumption was high. The researches mentioned above were not suitable for industrialization.

In this work, TiO₂ nanoparticle was prepared by sol-gel method and the factors of TiO₂ nanoparticle preparation, such as amount of distilled water and absolute ethyl alcohol, calcination temperature were investigated. It provide a theoretical reference about the preparation of TiO₂ nanoparticle by sol-gel method. Meantime, the effect of TiO₂ nanoparticle amount and the pH value on photocatalytic activity were also studied. It is suitable for industrialization due to the degradation of high concentration phenol



solution and low cost. It also provides a novel way for the treatment of coal-chemical wastewater.

2. Experimental

2.1 Preparation of TiO_2 nanoparticle

TiO_2 nanoparticle was prepared by sol-gel method. Tetrabutyl titanate (10mL) was mixed with absolute ethyl alcohol (50mL) under vigorous stirring for 30min, which obtained solution A. Subsequently, distilled water (5mL) was mixed with absolute ethyl alcohol (50mL) and glacial acetic acid (6mL) under rapidly stirring for 30min, which obtained solution B. At last solution A was added into solution B drop by drop under rapidly stirring. Thus, TiO_2 gel was obtained. The gel was aged at room temperature for 24 hours, followed by drying at 80 °C for 24 hours. After calcination in air at 575 °C for 4 hours, the obtained solid was grinded into particles, which was TiO_2 nanoparticle.

2.2 Photocatalytic Experiment

The photocatalytic experiments were carried out in a water-jacket reactor at a constant temperature of 10°C and initiated by irradiating with a 24W high-pressure mercury lamp ($\lambda=240\sim270$ nm), which was inserted in the phenol solution. In every experiment, 75mg of test sample and 150mL of 1×10^{-4} mg/L phenol solution were introduced in the reactor with magnetic stirring. 4mL of the irradiated solution was extracted from the reactor at certain intervals. After centrifugal separation, the concentration of phenol was analyzed by a UV-vis spectrophotometer at $\lambda=270$ nm.

3. Results and Discussion

3.1 Effect of factors of TiO_2 nanoparticle preparation.

In the same condition, the totally amount of absolute ethyl alcohol was 10mL, 30mL, 50mL, 70mL, 90mL, 110mL and 130ml, respectively. Obtained TiO_2 nanoparticle was employed to photodegrade the phenol solution. The results were showed in Figure 1. With the increasing amount of absolute ethyl alcohol, the degradation was kept sustainable growth until 90mL of ethyl alcohol added, the degradation reached the top of 73.8%. This is mainly due to the hydrolysis reaction of tetrabutyl titanate is rapid. Absolute ethyl alcohol slows down the hydrolysis reaction and narrows the diameter size of TiO_2 nanoparticle. Thus, the specific surface area is improved and activity sites per unite mass becomes more, which cause the photodegradation efficiency better. However, with the continuing increasing amount of absolute ethyl alcohol, the degradation declined. This is mainly due to excess absolute ethyl alcohol makes $Ti(OH)_x(OBu)_y$ do not touch each other. Thus, excess absolute ethyl alcohol do not generate gel and makes photodegradation efficiency worse.

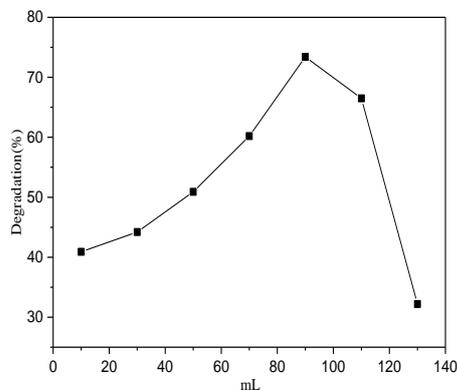


Figure 1. Effect of amount of absolute ethyl alcohol

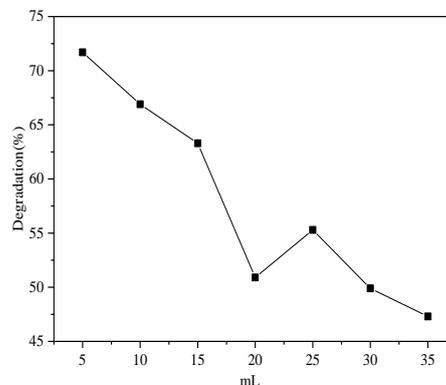


Figure 2. Effect of amount of distilled water

In the same condition, the amount of distilled water was 5mL, 10mL, 15mL, 20mL, 25mL, 30mL and 35ml, respectively. Obtained TiO_2 nanoparticle was employed to photodegrade the phenol solution. As

seen from Figure 2, at the beginning, 5mL of distilled water was added, the degradation reached the top of 74.8%. With the increasing amount of distilled water, the degradation of phenol declined. This is mainly due to the excess distilled water accelerates the hydrolysis reaction of tetrabutyl titanate. Excess distilled water generates agglomerate and precipitate, leading to the increasing of the diameter size of TiO₂ nanoparticle. Thus, it makes the photodegradation efficiency worse.

As-prepared TiO₂ were calcined at 300°C, 400°C, 500°C, 525°C, 550°C, 575°C and 600°C, after grinding, obtained nanoparticle was employed to photodegrade the phenol solution. The XRD patterns of the TiO₂ nanoparticle was shown in Figure 3. When the calcination temperature was 300°C, the as-prepared TiO₂ did not generate crystal. With the rising of temperature, the crystal was generated little by little and when the temperature reached at 500°C, anatase (A) was formed well. Whereafter, a little rutile (R) appeared at 575°C and became more than anatase at 600°C. The effect of calcination temperature on photodegradation was shown in Figure 4. With the rising of temperature, the degradation increased, reaching the top of 62.4% at 575°C, and then declined at 600°C. The reason of increasing degradation is that anatase, which was essential substance for photodegradation, formed gradually with the rising of temperature. The decline degradation at 600°C is mainly due to the rutile, which has low photocatalytic activity, became more than anatase. Thus, the activity sites decreased and degradation declined.

The structure and diameter size of TiO₂ nanoparticle was evaluated by SEM and the results were shown in Figure 5, TiO₂ nanoparticle was alveolate and compact, and the diameter size was about 20~50nm.

3.2 Photocatalytic activity test

10mg, 25mg, 50mg, 75mg, 100mg and 125mg of TiO₂ nanoparticle prepared were employed to photodegrade the phenol solution and the results were shown in Figure 6. With the increasing amount of TiO₂ nanoparticle, the degradation was improved until 75mg of TiO₂ added, the degradation reached 51.9%. However, it was declined with the continuing increasing amount of TiO₂ nanoparticle. The increasing degradation is due to the increasing amount of TiO₂ nanoparticle increases the number of photoactive sites and also more phenol molecules absorbed. Moreover, the decline degradation is due to the excess TiO₂ nanoparticle hinders the penetration of light and reduces the specific activity of the catalyst.

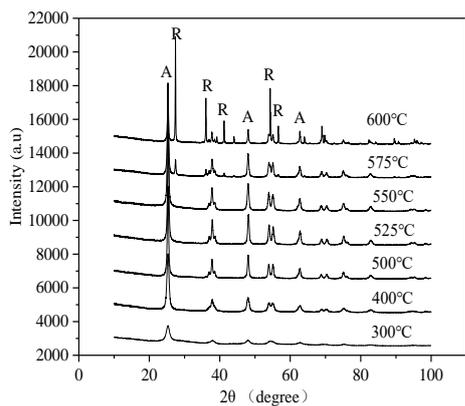


Figure 3. The XRD patterns of TiO₂ nanoparticle

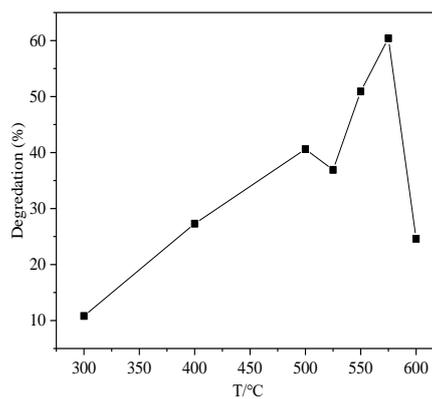


Figure 4. Effect of calcination temperature

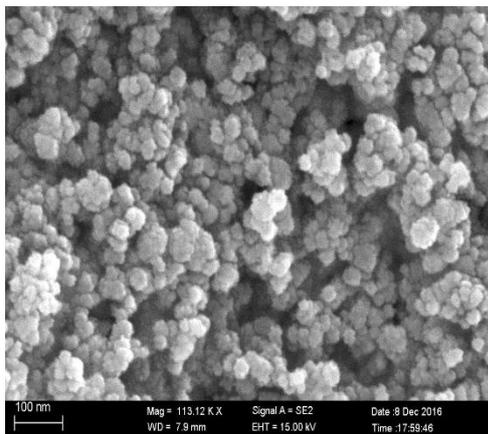


Figure 5. SEM of TiO₂ nanoparticle

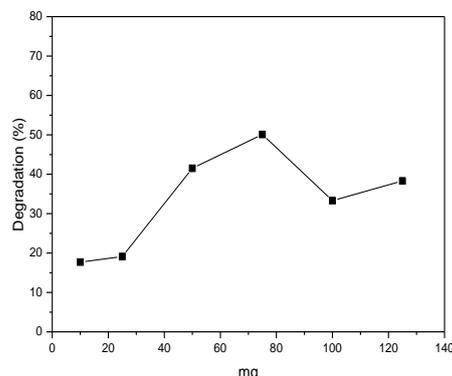


Figure 6. Effect of amount of TiO₂ nanoparticle

Hydrochloric acid and sodium hydroxide were employed to adjust the phenol solution pH value in 1, 2, 3, 4, 5, 6, 7, 8, and 9, respectively. Effect of phenol solution pH value was investigated and the results were shown in Figure 7. At the beginning, the degradation reached the top when pH value was 1 and then declined with the increasing of pH value, the highest degradation rate was 92.4%. According to previous reports [12, 13], the point of zero charge (pH_{pzc}) of TiO₂ is about 6.8. Thus, the TiO₂ surface is positively charged below this value and negatively charged above it. The results in Figure 7 indicate that the degradation is favored in an acidic solution, on the contrary, it is inhibited in a basic solution as compared with that of in neutral solution. In the acidic solution, phenol is primarily in its nonionic form, water solubility is minimized and the adsorption onto the catalyst is maximized. It is supposed that the density of •OH radicals is highest near the surface of TiO₂ nanoparticle and decreases rapidly with distance from the surface. At higher pH, phenol tends to exist as negatively charged phenolate species, which have extremely strong solubility in solution and do not be adsorbed on TiO₂ nanoparticle surface significantly. Also, more OH⁻ groups avoid the formation of •OH radicals, which have strong oxidizing property and play a significant role in the photodegradation of phenol. Moreover, high pH favors the formation of carbonate ions which are effective scavengers of OH⁻ ions. Through above results, the degradation efficiency is favorable in the acidic solution.

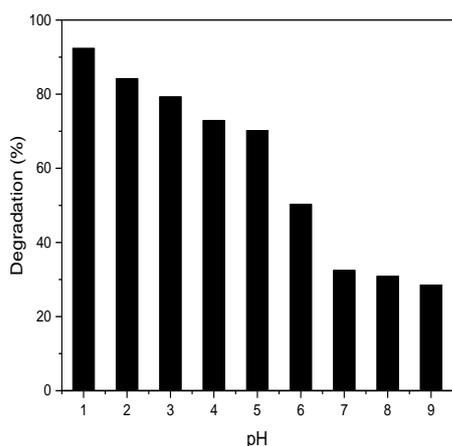


Figure 7. Effect of phenol solution pH value

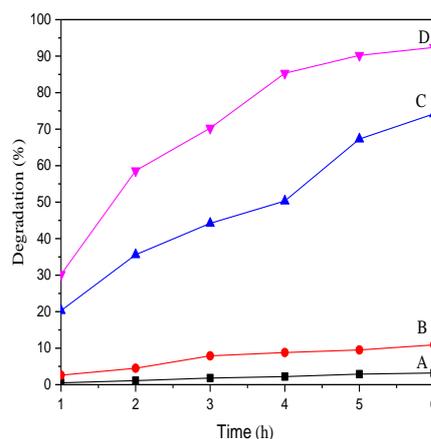


Figure 8. Comparison of degradation of phenol under different conditions

A: TiO₂ nanoparticle with dark, B: TiO₂ nanoparticle with visible light
 C: TiO₂ nanoparticle with UV D: TiO₂ nanoparticle with UV when pH value was 1

The photocatalytic activity of TiO₂ nanoparticle was evaluated by monitoring the degradation of phenol in aqueous solution. As shown in Figure 8, the degradation phenol was low in the dark and reached 5.2% after 6 hours, the low degradation rate is mainly ascribed to the adsorption of phenol on TiO₂ nanoparticle and TiO₂ was not excited. Under UV irradiation, the degradation of phenol was 10.6% at a given time, higher than that with dark, it is mainly due to the TiO₂ nanoparticle are excited by a little UV-light, which exists in visible light, and photodegrades the phenol. The degradation of phenol with UV-light and at the pH value 1 were 72.4% and 92.4%. The reason was explained above.

4. Conclusion

Factors of TiO₂ preparation were investigated and the optimal amount of distilled water and absolute ethyl alcohol and calcination temperature were 5mL, 90mL and 575 °C, respectively. In the photocatalytic activity test, 75mg of TiO₂ nanoparticle was best for photodegradation in 150mL of phenol (100mg/L) and degradation efficiency is favorable in the acidic solution. TiO₂ had a good performing of photodegradation of phenol solution and also had a potential application to the treatment of coal-chemical wastewater.

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