Study on the Photocatalytic Performance of Modified TiO$_2$

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Abstract. In this study, the modified TiO$_2$ was prepared by sol-gel and calcination method and the photocatalytic performance was studied by treating Methylene Blue simulated wastewater. The influence of the TiO$_2$ dosage and time, modified method of TiO$_2$, calcination temperature and calcination time on photocatalytic performance were examined. The FTIR of pure TiO$_2$ was tested. The results of FTIR showed that the bending and stretching vibration peaks of hydroxyl and O-Ti-O structure of TiO$_2$ were detected. The study indicates that modified TiO$_2$ is beneficial to the treatment of dye wastewater.

1. Introduction
Photocatalytic technology has been studied since 1972 [1]. Nano titanium dioxide (TiO$_2$) is recognized as the most effective photocatalyst because of non-toxic, tasteless and making organic pollutants degrade completely. However, TiO$_2$ has a wide band gap, and its light absorption is limited to the ultraviolet region. While the utilization of sunlight is also limited because the ultraviolet is too little from the spectrum. The modified methods of TiO$_2$ are studied in order to improve the utilization of TiO$_2$ in the field of pollutant treatment [2-3].

The dye wastewater is a very common organic wastewater. There are many kinds of organic pollutants in the wastewater, which has a serious impact on the survival of human beings, animals and plants. There are many ways to deal with it. The photocatalytic degradation of TiO$_2$ is effective to treat the dye wastewater. The organic of wastewater can be mineralized into carbon dioxide and water [4].

In this paper, the TiO$_2$ was prepared by sol-gel and calcination method. The modified methods of TiO$_2$ are also studied. The influence of the TiO$_2$ dosage and time, calcination temperature and calcination time on photocatalytic performance were tested.

2. Experimental

2.1. Materials
Tetrabutylorthotitanate (Ti(OBu)$_4$) as the titanium source was used to prepare TiO$_2$. Ethyl alcohol (CH$_3$CH$_2$OH) and acetic acid (CH$_3$COOH) were used as solvent and dispersing agent in the experiment, respectively. The ferric chloride (FeCl$_3$), carbamide (CO(NH$_2$)$_2$), thiourea (CH$_4$N$_2$S) were used as ferric, nitrogen and sulfur source, respectively. All reagents in the experiment were analytical grade (AR) and obtained from Tianjin Damao Chemistry Reagent Corporation, China.

The Methylene Blue in the study was dissolved with distilled water as the simulated waste water.
2.2. The Preparation of modified TiO$_2$

The modified TiO$_2$ was prepared using the sol–gel and heat-treatment method. The preparation process was as follows: First, 60mL acetic acid was added to 240mL ethyl alcohol in drops and stirred for 0.5h. Then 15mL distilled water was added. The solution was called solution A. In addition, 100mL Ti(OBu)$_4$ and 240mL ethyl alcohol were mixed together to stir 0.5h. That was called solution B. Finally, the solution A was added to solution B and the mixed solution was stirred for 1.0 h. Then the solutions of ferric chloride (FeCl$_3$), carbamide (CO(NH$_2$)$_2$), thiourea (CH$_2$N$_2$S) were separately added to the mixed solution according to a certain proportion to get the different methods modified TiO$_2$. (the percentage: Fe to Ti is 0.05%, N to Ti is 0.05% and S to Ti is 0.005%, respectively). During the preparation, ammonia water and hydrochloric acid were also added to control pH value of the solution and prevent the hydrolysis of ferric chloride. The co-doping mixed solution was stirred for 1.0 h and placed for 12h to form wet gel. Then the wet gel was dried at 100 °C for 10.0 h in the oven to form dry gel powder. Lastly, the dry gel powder was heated at a certain temperature for several hours. The prepared modified TiO$_2$ powder is stored in a desiccator for photocatalytic degradation reaction. For comparison, the pure TiO$_2$ and Fe-N co-doping TiO$_2$ were also prepared using a similar method.

2.3. The experiment of photocatalytic degradation

The photocatalytic experiment was carried out in the self-made reactor. A certain amount of TiO$_2$ is added into the conical flask with 5mg/L Methylene Blue solution. After 30 minutes in dark, the photocatalytic degradation was carried out under UV light. The 15mL supernatant was withdrawn and centrifuged at regular intervals. Degradation of Methylene Blue solution was calculated by examining the absorbance of Methylene Blue solution at their maximum absorbance (664 nm) in a 722N visible spectrophotometer.

The degradation rate (%) of Methylene Blue solution is calculated according to the following formula:

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\text{degradation rate} \text{ (%) } = \left( \frac{A_0 - A}{A_0} \right) \times 100\% \quad (1)
\]

Where $A_0$ is the initial absorbance of solution Methylene Blue. $A$ is the absorbance of solution Methylene Blue at any time.

2.4. The FTIR of pure TiO$_2$

The Fourier transform infrared (FTIR) spectra of the pure TiO$_2$ was obtained on a Perkin Elmer spectrum 100. The powder samples were mixed with KBr of spectroscopic grade and pressed into disks 10 mm in diameter and 1 mm thick. The samples were scanned in the spectral range of 500–4000 cm$^{-1}$.

3. Result and Discussion

3.1. Result and Discussion

Fig. 1 shows the effect of TiO$_2$ dosage on the photocatalytic degradation Methylene Blue. The degradation rate increases with the increasing of TiO$_2$ dosage. The degradation reacted rapidly in the early stage of the reaction. The degradation rate is nearly stable when the reaction reaches 300min. The degradation rate of 2g/1000mL TiO$_2$ is almost up to 20%, however, that of 4g/1000mL TiO$_2$ is 27%. In view of saving material, 2g/1000mL TiO$_2$ is chosen for later experiment.
Figure 1. Effect of TiO$_2$ dosage and time on photocatalytic degradation experiment

FTIR spectra of pure TiO$_2$ samples is shown in Figure 2. The two peaks near 1650cm$^{-1}$ and 3500–3000cm$^{-1}$ belong to the bending and stretching vibration peaks of TiO$_2$ surface hydroxyl groups. 650 cm$^{-1}$ (300-800cm$^{-1}$) near the absorption peak belongs to O-Ti-O TiO$_2$ structure.

Figure 2. FTIR sample of pure TiO$_2$

3.2. The photocatalytic performance of modified TiO$_2$

Figure 3 shows the photocatalytic performance of modified TiO$_2$ for the simulated waste water of Methylene Blue. The TiO$_2$ of different methods modified were calcined at 450$^\circ$C for 1 hour. The simulated waste water of Methylene Blue is hardly degraded under the pure ultraviolet light. The photocatalytic performances of modified TiO$_2$ by different methods have been improved in different degrees. Fe-N-S co-doping TiO$_2$ has the highest photocatalytic performance. This phenomenon is due to the charge imbalance is caused by the excessive positive charge when Ti$^{4+}$ in TiO$_2$ is replaced by S$^{6+}$ ions. Then, lots of hydroxyl ions are easily adsorbed on the surface of TiO$_2$ which is benefit to produce hydroxyl radical. The hydroxyl radicals may play a role in the degradation of Methylene Blue [5]. Furthermore, the red shift of absorption band of TiO$_2$ is caused by Fe-N modified. Therefore, Fe-N-S co-doping TiO$_2$ shows very good photocatalytic performance.
3.3. Effect of calcination temperature on photocatalytic performance of modified TiO$_2$

Fig. 4 shows that the degradation rate (%) of the simulated waste water of Methylene Blue increases from 400°C to 500°C. However, the degradation rate decreases when the calcination temperature exceeds 500°C. It can be explained that the crystalline of TiO$_2$ is transformed from amorphous to anatase with the increase of temperature. And the anatase TiO$_2$ crystal has better photocatalytic activity, which makes the degradation rate improve immediately. The grain size of TiO$_2$ becomes larger when the calcination temperature continues to increase, then the photocatalytic activity of TiO$_2$ decreases.

3.4. Effect of calcination time on photocatalytic performance of modified TiO$_2$

Figure 5 shows that the effect of calcination time on photocatalytic performance of modified TiO$_2$. It can be seen that the modified TiO$_2$ has the best photocatalytic performance for calcination 1-2h. The photocatalytic performance decreases with the increasing of calcination time which is due to that the grain size of TiO$_2$ becomes larger.
4. Conclusion
The pure and modified TiO₂ are produced by Sol-gel and calcination method. The degradation rate of the simulated wastewater of Methylene Blue quickly increases in the begin of reaction. The bending and stretching vibration peaks of hydroxyl and O-Ti-O structure of pure TiO₂ were detected by FTIR. The modified TiO₂ has better photocatalytic performance. Especially, the photocatalytic performance of Fe-N-S modified is better than others. Meanwhile, the photocatalytic performance of modified TiO₂ can be influenced by calcination temperature and time. The optimum conditions are: calcination temperature 500℃ and time 1-2h.

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