

Study on the Photocatalytic Removal of Styrene in Water

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Abstract: With the development of economy in China, especially energy, petrochemical industry, the amount of water transportation of chemicals is increasing day by day. At the same time, the chemical leakage probability is greatly increased, and it also affects people's daily life and health. In this study, we modify the titanium dioxide using other materials and the light utilization rate and photocatalytic activity of TiO₂ is improved. We also apply it in the disposal of styrene in the river water and achieved good results. In addition, the catalytic effect of various catalysts was compared, and the effect of different conditions to the reaction is also researched.

Introduction

As the development of economy in China, especially energy, petrochemical industry, the amount of water transportation of chemicals is increasing day by day. At the same time, the chemical leakage probability is greatly increased which affects people's daily life and health. In order to control and manage all kinds of pollutants to the environment, governments and researchers have made a lot of efforts to develop new technologies.

In last century, the Japanese researcher found that the titanium dioxide could decompose water. From that time, photocatalytic materials have been attracted great interest. In order to improve the photocatalytic efficiency of photocatalyst, many scientists have carried out a lot of research and exploration. Among them, there are some common photocatalysts, such as TiO₂, CdS, ZnO, WO₃, SnO₂, and so on. [1-5] TiO₂ has good optical and electronic properties, such as low cost, high catalytic performance, stable chemical properties and low toxicity. It has been widely studied and applied to the degradation of various pollutants. In order to improve the shortcomings, many scholars have made a modification of the titanium dioxide. First, the researchers mixed the N element and shortened the band-gap successfully. [6] Others found that the doping of Fe ions can significantly decrease the recombination rate of the hole. [7] Furthermore, someone added bentonite to TiO₂, the result showed that the specific surface area, thermal stability, cation exchange property of TiO₂ were significantly increased, and the catalytic efficiency was improved. [8]

In this study, we modify the titanium dioxide using other materials and the light utilization rate and photocatalytic activity of TiO₂ is improved. We also apply it in the disposal of styrene in the river and achieved good results. In addition, the catalytic effect of various catalysts was compared, and the effect of various conditions on the reaction is researched.

Experimental Procedure

Materials Preparation

Tetrabutyl titanate (24.0ml) is doped into the mixture of 4.0ml glacial acetic acid and 90.0ml absolute ethyl alcohol. Keep agitate and get solution A. Then use 1.0ml hydrogen nitrate to mix up with 10.0ml deionized water and get solution B. Solution B is dropped into solution A slowly and keep agitate. Later, the transparent sol will form. Drop urea into the mixture (Ti/N=2) slowly and keep agitate. Then use the same procedure with 2.1 to get products. The N-TiO₂ photo-catalyst was obtained. Use the same method to get Fe-TiO₂ photo-catalyst, Bentonite-TiO₂ photo-catalyst using iron (III) nitrate (Ti/Fe=5) and 20ml bentonite solution. All the samples are calcined at 600°C.

Material Characterization

XRD

The XRD results of TiO_2 (calcined at 600°C) and modified TiO_2 including Fe- TiO_2 , N- TiO_2 and Bentonite- TiO_2 are showed in Figure 1. The diffraction peak of TiO_2 is relative to the standard X-ray of TiO_2 , and the crystal phase of the film is anatase. It has a high (101) orientation, which indicates that TiO_2 has formed a certain ordered crystal structure. According to the X-ray line width method, the particle size of anatase TiO_2 particles in the film was about 15 nm. The crystal of 15 nm anatase phase has photo-catalytic activity, and it is also a prerequisite for obtaining smooth film.

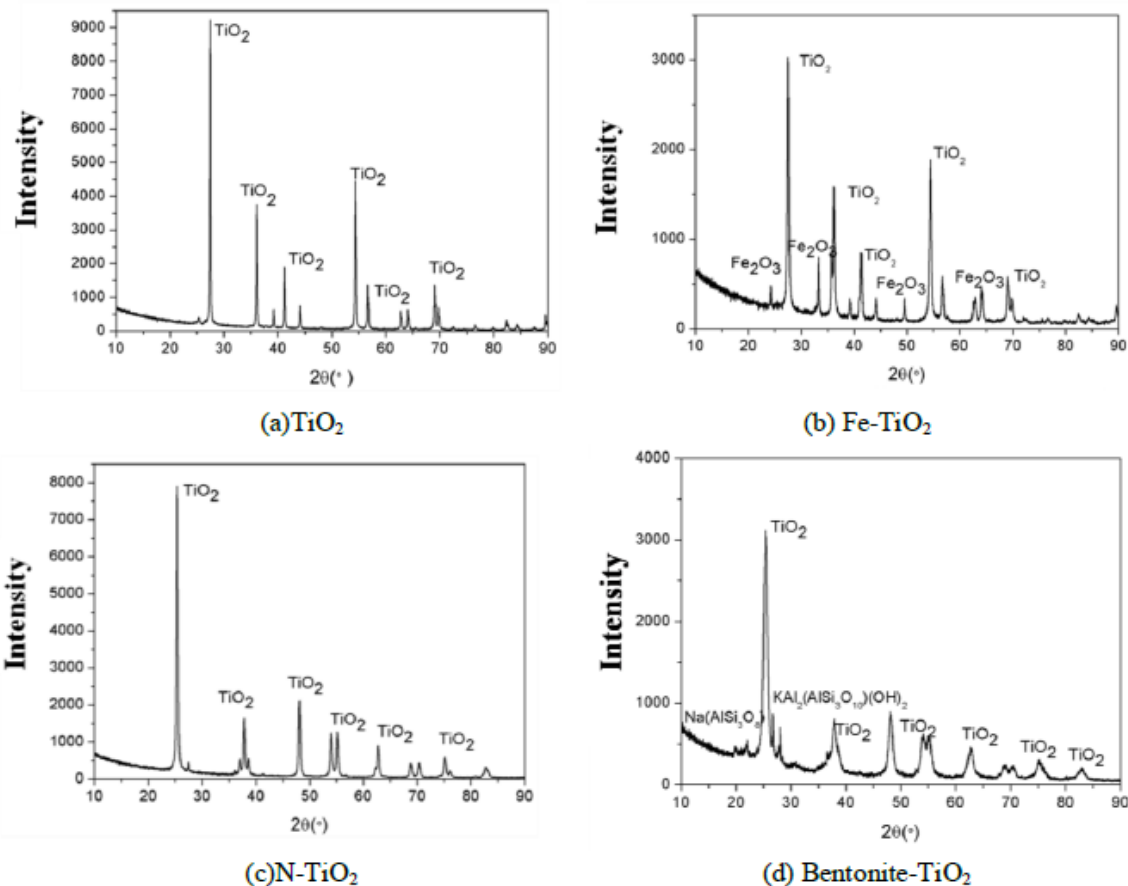


Figure1 The XRD results of different photocatalysts

BET

The results show that the specific surface area of TiO_2 is gradually decreased with the increase of calcination temperature. But the surface area increased after other materials doped. In particular for bentonite- TiO_2 , the surface area almost reached the level of commercial titanium dioxide. So the specific surface area of doped photo-catalyst material is more significantly improved than single TiO_2 .

SEM

The experimental results show that the particles of care gradually increased as the calcination temperature increasing. The product of TiO_2 is more uniform, but with the increase of calcination temperature, the particles of TiO_2 are obviously uneven and the particles are obviously increased. And the particles of other doped materials which calcined at 600 degree are more uniform, smooth and smaller. It reveals that crystal structure of the doped photo-catalyst material are uniform than single TiO_2 , and it may improve the catalytic effect of photo-catalyst. Of course, the particle

morphology of different doping samples is different.

Photo-catalytic Degradation Reaction

The styrene solutions of different concentration are prepared respectively. Then different kinds of catalysts are added into styrene solution. At the same time, keep agitate and open the UV lamp. Finally, the samples are centrifugal separated at different time. The level of styrene is measured by purge and trap GC-MS.

Results and Discussion

Different Photocatalysts

In this experiment, the water solution of the catalytic material is added to the pure styrene solution and keep agitate at room temperature. At the same time, the ultraviolet light is turned on. Get the reaction liquid at 0, 5, 10, 20, 40, 60 and 80 minutes, then centrifugal for 3 minutes and take the supernatant. The styrene concentration is determined by gas chromatography-mass spectrometry. The initial pH value of the solution is about 7.5, and the pH value of the solution is 6.5 ± 0.3 after the reaction.

The result shows out that styrene degradation rate increased as the reaction time increasing generally in Figure 2. And the degradation efficiency of doped TiO_2 is better than TiO_2 and the best is bentonite- TiO_2 . As the results of previous studies, nitrogen doping can increase the absorption of visible light in our research. Nitrogen entering into the titanium dioxide lattice can move its absorption edge to the visible range. This is because the Nitrogen doping could produce an intermediate band gap to shorten the gap in the valence band top. For Fe^{3+} doped TiO_2 , it shows a strong visible light absorption. This is because Fe^{3+} doping can form an impurity level in the band gap of TiO_2 . The bentonite can absorb a part of the visible light and its big specific surface area is also benefit to the reaction. The result also confirms that the effect of modified photo-catalyst is better than pure TiO_2 .

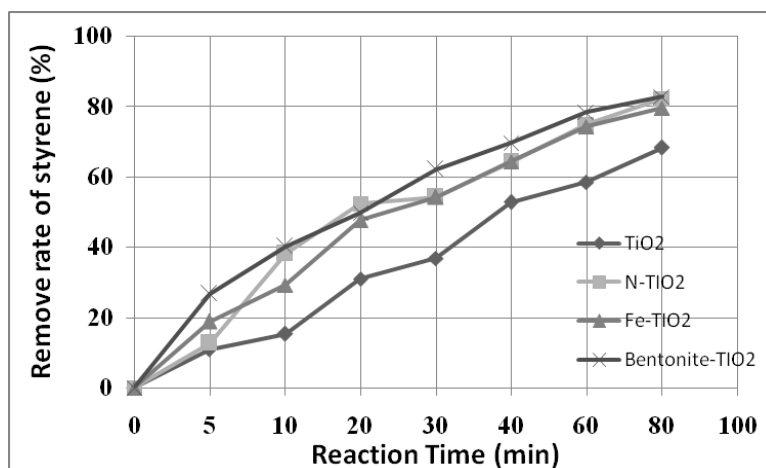


Figure 2 The results of using different photo-catalysts

The Influence of Lighting Time

In this part, we use the best materials of Bentonite- TiO_2 which selected from the above experiment. The experiment procedure is basically the same as 3.1, but the UV irradiation time is 0, 20, 40, 60, 80 min. The result reveals that styrene degradation rate increased as the reaction time and also lighting time increasing in Figure 3. Generally, the degradation rate increased significantly at the beginning. After the illumination time is up to 60 minutes, although the photolysis rate is still increasing, the trend is tends to be gentle. Researcher suggests that the wettability can be changed

under UV irradiation no matter polycrystalline or single crystal surfaces of anatase and rutile.^[9] With the increase of illumination time, the contact angle of the membrane and water gradually becomes smaller, and the catalytic activity increases gradually. When it up at a certain time, the contact angle will not decrease as the light time increasing, thus the catalytic activity of the membrane becomes stable. As the lighting time increasing, the catalytic activity increases gradually. After a certain time, the catalytic activity will be stable.

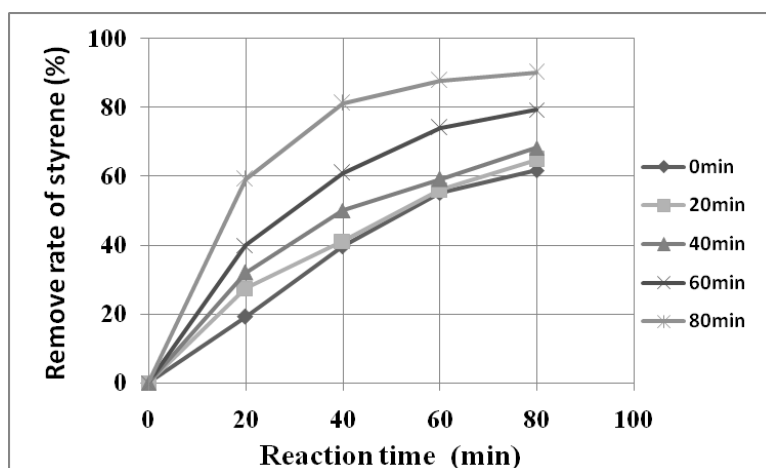


Figure 3 The influence of lighting time

The ultraviolet light emitted by the high pressure mercury lamp is stronger than natural light, so the photon energy is greater than or equal to the band gap energy of TiO_2 . When the light radiate to the TiO_2 , the electronics in the valence band can be excited into the conduction band to generate electron-hole pairs, and a series of reaction will take place on the surface. Finally, the free radicals will be generated, so that the organic compound will be degraded to CO_2 and H_2O .^[10-13] when the photon energy is stronger, the degradation effect is more obvious. So the photo-degradation rate of chemicals is higher under mercury lamp than sunlight. But in the practical application, it is feasible to use solar energy and it is also to the economic point.

The Influence of Reaction Temperature

In this part, experiments of different reaction temperatures were carried out using the best materials selected in the former experiment. The method is the same as above, but the reaction temperature is 25 degrees and 35 degrees. The removal effect of photocatalyst in different reaction temperatures is shown in Figure 4. The result shows that the chemical removal effect is better under reaction temperature of 35 degrees than 25 degrees. As the degradation reaction is endothermic reaction, the temperature rise will inevitably accelerate the reaction. It can be concluded that when the chemical leakage occurs in the condition of high temperature, the effect of photocatalytic degradation of chemicals will be more obvious.

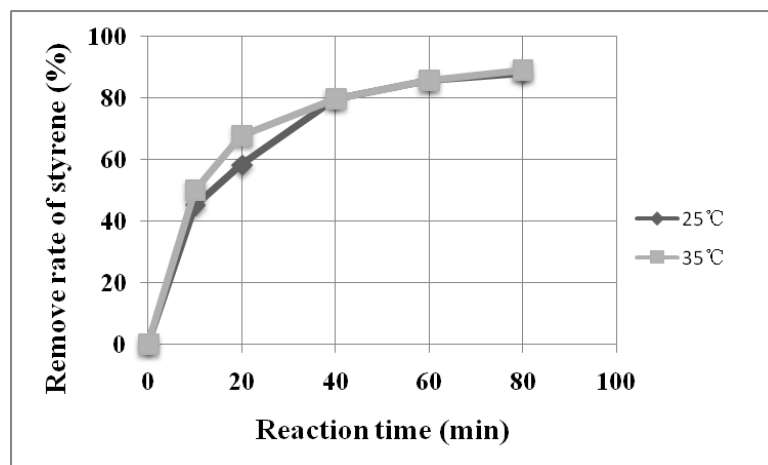


Figure 4 The influence of reaction temperature

The Influence of Concentration and Reaction Type

Researchers suggest that the degradation rate was related to the initial concentration of reactants. The initial concentration of styrene in solution is inversely proportional to the rate of photolysis. It reveals that the photocatalytic technology is an effective method to deal with the low content of organic pollutants. The effect of the concentration of reactant on the degradation rate is similar to the effect of the intensity of the light intensity. The rate equation of heterogeneous photocatalytic degradation can be expressed as the Langmuir-Hinshelwood kinetic equation. The kinetic equation of the photocatalytic reaction shows that when the reaction concentration is low, the reaction is in accordance with the law of first order kinetics, that is, the degradation rate is proportional to the concentration. When the reactant concentration increased to a certain degree, the reaction rate increased with the increase of the concentration of the reactants. But this increase is not proportional to the concentration of reactants. Then, as the increase of concentration, the reaction rate will not change with the concentration.

Conclusions

In this work, the doped TiO_2 is applied in styrene photo-catalytic remediation. Different kinds of catalysts were used, and the degradation rate of styrene was researched under different conditions. The results revealed that the styrene removal percentage increased as the reaction time increasing generally. For the four types of catalysts, the efficiency of bentonite- TiO_2 is the best. Furthermore, the styrene degradation rate increased as the lighting time increasing. Finally, the styrene degradation rate was accelerated as the reaction temperature increasing.

When some organic material has a strong UV absorption, high concentration of organic matter will shield the ultraviolet radiation of the catalyst, which can affect the photocatalytic efficiency. Therefore, the photocatalytic method is suitable for the treatment of slightly polluted water. In inland chemicals leakage accident treatment, other methods should be used first to reduce pollutant content and then use photocatalyst method to treat rest of pollutants for the economic point. Thus, the effect of water treatment and the economic benefit will be improved obviously.

Acknowledgements

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