Study on the effect of Fe and N co-doped supported TiO$_2$/GF photocatalytic oxidation of nitrobenzene wastewater

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Abstract. This research aims to treat the refractory nitrobenzene wastewater in the industrial water treatment industry with modified supported TiO$_2$, and to study its influence on the treatment effect. Experiments have found that by preparing Fe and N co-doped TiO$_2$/GF supported catalysts, it has better catalytic performance. Under the same conditions, Fe and N co-doped TiO$_2$/GF can degrade nitrobenzene wastewater better than single doped with Fe-TiO$_2$/GF and N-TiO$_2$/GF, the removal rates of nitrobenzene and COD are as high as 97.2% and 92.5%, respectively. The Fe and N co-doped TiO$_2$/GF catalyst overcomes the agglomeration of traditional powdered TiO$_2$ in solution, and has a good removal effect on nitrobenzene wastewater.

1 Research background and significance

Photocatalysis is a new advanced oxidation technology with simple equipment, mild conditions, and obvious effects of oxidizing and degrading organic matter. It can convert organic matter into water and carbon dioxide by using the energy of sunlight, which can meet environmental protection requirements. Inorganic metal oxide semiconductor materials are commonly used photocatalysts, and TiO$_2$ has become an ideal photocatalyst due to its stable chemical properties, non-toxicity, and low cost. There are three main crystal types of TiO$_2$: anatase, rutile, and brookite. A large number of studies have shown that anatase is the most active crystal type, and its energy gap is equivalent to the photon energy with a wavelength of 387.5 nm.

Frank and Bard pioneered the application of semiconductor materials to sewage treatment, and cyanate oxide used TiO$_2$ as a photocatalyst. TiO$_2$ photocatalytic oxidation technology is considered to be one of the most promising photocatalytic materials at this stage.

Nitrobenzene wastewater is a key and difficult point in the industrial water treatment industry. In order to solve the harmful effects of nitrobenzene wastewater on people's production and life, domestic and foreign scholars have conducted a lot of research on the treatment methods of nitrobenzene wastewater. Shang Xiaoyuan used the biodegradation method to study the granulation of aerobic sludge and the removal effect of granular sludge on nitrobenzene wastewater. The experimental results showed that the removal rate of TD was not ideal. Yang Pengfei conducted experiments with physical treatment methods. The experimental research showed that the removal rate of wastewater is not affected by the pH of the solution. At the same time, the extraction phase can be regenerated and used for multiple extractions. However, some industrial extractants are organic solvents, which are easy to be used in wastewater. Cause secondary pollution, and the treatment effect is not thorough enough.

This study mainly studies the preparation conditions of Fe and N co-doped TiO$_2$/GF photocatalysts and the process conditions for the treatment of nitrobenzene wastewater, which provides a basis for accelerating the industrial use of photocatalytic oxidation technology.

2 Materials and methods

2.1 Test device and test carrier

The photocatalytic oxidation device used in the experiment is self-made, which is composed of light source, reaction device and aeration device. The glass fiber used in the experiment is linear AR glass fiber, also known as alkali-resistant glass fiber, which is 100% inorganic fiber.

2.2 Experiment method

In this experiment, the Fe and N co-doped TiO$_2$/GF photocatalysts were prepared by the sol-gel/dipping-climbing method. At the same time, the ultraviolet mercury lamp with a wavelength of 253.7 nm and 45 W was used as the light source to investigate the different ion doping in the preparation process. The impurity amount and doping type affect the performance of TiO$_2$/GF supported photocatalyst, and the optimal doping amount is determined.

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3 Results and discussion

Test standard conditions: 45W ultraviolet lamp, 0.15g supported photocatalyst sample, 1000ml nitrobenzene concentration is about 78.86mg/L, COD concentration is about 1582mg/L. The supernatant was taken to determine the absorbance at 545nm and 465nm.

3.1 The effect of nitrogen doping on the treatment effect

Keep other benchmark conditions unchanged, weigh 0.15g nitrogen-doped TiO\textsubscript{2} containing n(N):n(Ti) ratios of 0.05, 0.1, 0.2, 0.4, 0.6, and the benchmark conditions of the photocatalysis test remain unchanged, calculate The removal rate of nitrobenzene and COD, draw a curve, and investigate the effect of different nitrogen doping on the catalytic performance. The test results are shown in Figure 1 and 2:

![Figure 1](image1.png)

**Fig1.** Influence of nitrogen content on removal of nitrobenzene in wastewater

![Figure 2](image2.png)

**Fig2.** Influence of nitrogen content on COD removal in wastewater

The test results show that under the same reaction conditions and within the same reaction time, different doping amounts of N have little effect on the catalytic removal of wastewater. When the ratio of n(N):n(Ti) is 0.2, the catalytic performance of N-TiO\textsubscript{2}/GF photocatalyst is the best, and the removal rate of nitrobenzene and COD reaches the maximum of 90.6% and 78.9%, respectively.

3.2 The influence of iron content on the treatment effect

The benchmark conditions of the photocatalysis test remain unchanged. Weigh 0.15g of iron-doped TiO\textsubscript{2} containing n(Fe):n(Ti) to 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, and calculate the nitro group. The removal rate of benzene and COD, draw a curve, and investigate the influence of different iron doping amounts on the catalytic performance. The test results are shown in Figure 3 and 4:

![Figure 3](image3.png)

**Fig3.** Influence of iron content on removal of nitrobenzene in wastewater

![Figure 4](image4.png)

**Fig4.** Influence of iron content on COD removal in wastewater

The test results show that the catalytic effect of Fe-TiO\textsubscript{2}/GF photocatalyst is better than that of N-TiO\textsubscript{2}/GF photocatalyst. With the increase of Fe doping concentration, the catalytic removal effect of wastewater first increases and then decreases. When the concentration reaches the ratio of n(Fe):n(Ti) to 0.9%, the catalytic effect is the best, and then when the concentration increases again, the catalytic removal effect decreases.

3.3 Orthogonal test

The optimal preparation conditions of Fe and N co-doped TiO\textsubscript{2}/GF photocatalyst and its treatment effect on nitrobenzene wastewater were determined by four-factor three-level orthogonal experiment. Orthogonal test design: The experiment selects four influencing factors: Fe doping amount, N doping amount, calcination time and calcination temperature, each of which takes 3 level conditions, and the design adopts L\textsubscript{3}(3\textsuperscript{4}) orthogonal test.
It can be seen from the orthogonal test that the doping ratio of iron and nitrogen has different effects on the performance of the photocatalyst. The order of the influence of each influencing factor on the photocatalytic performance of the catalyst is: calcination temperature > Fe doping amount > N doping amount > calcination time. There are optimal preparation conditions for each influencing factor: calcination time 2h, calcination temperature 450°C, Fe doping amount n(Fe): n(Ti) ratio is 0.7% (molar fraction) and N doping amount n(N) : n(Ti) is 0.4% (molar fraction), and the removal rate of nitrobenzene wastewater reaches 97.5%.

4 In conclusion

(1) Under the same reaction conditions and the same reaction time, different doping amounts of N have little effect on the catalytic removal of wastewater. When the ratio of n(N):n(Ti) is 0.2, the catalytic performance of N-TiO$_2$/GF photocatalyst is the best, and the removal rate of nitrobenzene and COD reaches the maximum of 90.6% and 78.9%, respectively.

(2) The catalytic effect of Fe-TiO$_2$/GF photocatalyst is better than that of N-TiO$_2$/GF photocatalyst. When the doping concentration reaches 0.9% of n(Fe):n(Ti), the catalytic effect is the best.

(3) The doping ratio of iron and nitrogen has different effects on the performance of the photocatalyst. There are optimal preparation conditions for each influencing factor: the calcination time is 2h, the calcination temperature is 450°C, the ratio of Fe doping amount n(Fe): n(Ti) is 0.7% (molar fraction) and N doping amount n(N): n(Ti) is 0.4% (molar fraction), and the removal rate of nitrobenzene wastewater reaches 97.5%.

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