Orthogonal design Fe, N co-doped TiO₂/GF photo catalyst treatment of nitrobenzene wastewater.

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Abstract. Objective: to determine the optimum preparation conditions and the treatment effect of TiO₂/GF photo catalyst by four factors and three horizontal orthogonal tests. Methods: the preparation of sol-gel immersion Fe, N total light catalyst, doping TiO₂/ GF in homemade photo catalytic reactor, based on nitrobenzene degradation rate, design and discusses the calcination time, calcination temperature, Fe doping amount and N doping amount of light the influence of catalyst preparation and its physical and chemical properties. Results: the results showed that the main order of influence was: >Fe doping, >N doping, > calcination time; The catalytic activity of co-doped photo catalyst is better than that of single doped TiO₂ catalyst. Conclusion: the best preparation conditions as follows: 2.5 h calcination time, calcination temperature 550 °C, Fe doping amount 0.5% (mass fraction) and N doping amount is 0.45% (mass fraction), deal with 40 mg/L of nitrobenzene degradation, nitrobenzene wastewater degradation rate was 86.5%. The catalyst can be reused.

1. Introduction
As the country's industrial production level and the continuous improvement of people's living standard, in the pursuit of high quality life quality at the same time, we is heavily influenced by the pollution of water environment, for the green deal effectively with light push organic wastewater pollution, scholars at home and abroad to the methods of physical [1], biological [2] and chemical [3] degradation process and obtain certain effect. The photochemical oxidation technology is a new advanced chemical oxidation technology for treating wastewater with high efficiency. Through a large number of studies have found that pure TiO₂ photo catalyst is high activity, good stability, oxidation without selectivity and low cost, but its light response range is narrow, only under uv irradiation have a higher removal rate, but also difficult to recycle powder TiO₂ [4-6]. Therefore, it is of practical significance to apply the TiO₂ catalyst load to the carrier to realize repeated utilization and modify it to broaden its absorption spectrum.

TiO₂ will load on the carrier use ion modified TiO₂ light catalyst is one of the most important method to improve the photocatalytic activity of TiO₂, mixed with metal ions can have the effect of extending the TiO₂ light response range[7],Marui[8] use different iron ion content of TiO₂ nano powder through water preparation of iron ions doped Ti polyure O₂ nanotubes in ultraviolet light - methylene blue solution study found that when the iron doping amount is 1 mol %, 200 °C under the reducing atmosphere sintering the TiO₂ nanotubes photocatalytic effect is best. Iron ion doping
enhanced photocatalytic performance without affecting the growth direction of nanotubes, and the degradation efficiency was greatly improved. And non-metallic composite ion inhibition photo production carriers[9], 2001 Asahi in Science is put forward for the first time such as nitrogen doping replace TiO$_2$ that TiO$_2$ may narrow band gap, a small amount of lattice oxygen made his TiO$_2$ visible light activity, increase the efficiency of the light source. Duan Xiuquan [10] using solvent hot method, combine nitrogen doped TiO$_2$ and heterostructure, whether in the uv or under visible light irradiation, the preparation of nitrogen doped TiO$_2$ heterostructure samples than goods TiO$_2$ Degussa P25 has higher photocatalytic efficiency. Miao Guashuai [11] was tested with iron iodine; Zinc fluoride; The study found that the treatment effect of co-doping was significantly higher than that of single doping, and the synergistic effect of metal and non-metal was improved, and the photocatalytic performance of TiO$_2$ was improved.

In view of this, this experiment adopts the sol-gel method, the economic non-toxic urea, nitric acid iron doped glass fiber (GF) in load of TiO$_2$ photo catalyst, through orthogonal experiment, optimizing the preparation of Fe, N total light catalyst, doping TiO$_2$ / GF in homemade photocatalytic reactor, on the basis of nitrobenzene degradation rate, and the influence of various reaction conditions on the treatment effect.

2. Test section

2.1. Reagents and instruments.
The main instruments used in the experiment are shown in table 1.

| No. | Name                                      | Model   | Manufacturer                                |
|-----|-------------------------------------------|---------|---------------------------------------------|
| 1   | UV-visible spectrophotometer              | UV-9100 | Beijing Rayleigh analytical instrument co. LTD. |
| 2   | PH meter                                  | Hi 98127| Beijing hanakoyi technology co. LTD.         |
| 3   | Electric heating constant temperature      | DHG-9140A | Shanghai jinghong test equipment co. LTD. |
|     | drying oven                               | HH-4    | Shenyang electric furnace factory.          |
| 4   | Muffle furnace                            |         | Shanghai precision science instrument co. LTD. |
| 5   | Electronic analytical balance             | FA1004N | Jiangsu taixian Meiji wireless power plant. |
| 6   | Magnetic stirrer                          | GSP-77-03| Rigaku (science), Japan.                    |
| 7   | X-ray diffractometer                      | D/Max-III A | Jiangsu jiangyin lamps and lanterns factory. |
| 8   | Ultraviolet sterilizing lamp              | 20w     |                                             |

The main reagents and drugs used in the test are shown in table 2.
Table 2. The main reagents and medicines of the experiment

| No. | Name               | Level              | Manufacturer                                           |
|-----|--------------------|--------------------|--------------------------------------------------------|
| 1   | 30%H2O2            | Analysis of pure   | Shenyang xing hua reagent factory.                    |
| 2   | Tetra-butyl titanate | Analysis of pure   | China pharmaceutical group chemical reagent co. LTD.  |
| 3   | Potassium dichromate | Analysis of pure   | Shenyang shen yi fine chemicals co. LTD.              |
| 4   | Acetyl acetone     | Analysis of pure   | China pharmaceutical group chemical reagent co. LTD.  |
| 5   | Anhydrous ethanol  | Analysis of pure   | Beijing chemical reagent co. LTD.                     |
| 6   | The glass fiber    | Analysis of pure   | Shenyang xing hua reagent factory.                    |
| 7   | The urea           | Analysis of pure   | Tianjin feng shi chemical reagent technology co. LTD. |
| 8   | Distilled water    |                    | homemade                                               |

2.2. Preparation of Fe/N-TiO2 photo catalyst.

Sol-gel method[12] Fe/N doping TiO2/GF: room temperature, 30 ml of anhydrous ethanol and A certain quality of Fe(NO3)·9H2O in 250 ml beaker, chase under magnetic stirring drop join 20ml tetrabutyl titanate and 1.4ml acetyl acetone chelating agent, and continued to 300 rad/min speed under magnetic stirring 30 min, get A light yellow transparent liquid; At the same time, the preparation of anhydrous ethanol: water: the volume of acetic acid is for 10:4:1 mixture, add a certain quality of urea under magnetic stirring and 0.05 g coagulant aid PEG, 15 min after get B transparent solution; Add the B solution slowly to A solution, and then mix it uniformly and continuously for 1h, forming A transparent sol gel. Room temperature aged 12h. The preparation process of specific Fe/N-TiO2/GF is shown in figure 1.

![Diagram of sol-gel method](image)

Figure 1. Preparation of Fe/N-TiO2/GF.
3. Results and discussion

3.1. Optimization of catalyst preparation.
Orthogonal test design: the design of experiment adopts four factors three levels to investigate catalyst preparation process of catalyst ion ratio of inner defect position and the influence of calcination method on its external crystal structure, thus affecting the activity of photo catalyst.

Table 3. Orthogonal design table of factor conditions.

| Level | Value of each factor | Value of each factor | Value of each factor | Value of each factor |
|-------|----------------------|----------------------|----------------------|----------------------|
|       | Calcination time (h) | Calcination temperature (℃) | Fe doping ratio (%) | N doping ratio (%) |
| 1     | 2.5                  | 500                  | 0.4                  | 0.25                 |
| 2     | 4                    | 550                  | 0.5                  | 0.45                 |
| 3     | 5.5                  | 600                  | 0.6                  | 0.65                 |

Orthogonal test analysis: the final sampling centrifugation was performed after 2h of photocatalytic reaction. The orthogonal test results are shown in table 4. Table 5 data processing results. The greater the R value, the greater the influence of this factor on the experimental results. The results showed that the main order of the influence factors on the photocatalytic performance of the catalyst were: >Fe doping, >N doping, > calcination time. Through the analysis of variance, there were various influencing factors of the optimal preparation conditions: 2.5 h calcination time, calcination temperature 550 ℃, Fe doping amount 0.5% (mass fraction) and N doping amount is 0.45% (mass fraction), the degradation of nitrobenzene wastewater rate up to 86.5%.

Table 4. Orthogonal test results.

| NO. | Calcination time (h) | Calcination temperature (℃) | Fe doping ratio (%) | N doping ratio (%) | Degradation rate (%) |
|-----|----------------------|-----------------------------|---------------------|------------------|----------------------|
| 1   | 2.5                  | 500                         | 0.4                 | 0.25             | 63.8                 |
| 2   | 2.5                  | 550                         | 0.5                 | 0.45             | 86.5                 |
| 3   | 2.5                  | 600                         | 0.6                 | 0.65             | 40.7                 |
| 4   | 4                    | 500                         | 0.5                 | 0.65             | 55.2                 |
| 5   | 4                    | 550                         | 0.6                 | 0.25             | 72.5                 |
| 6   | 4                    | 600                         | 0.4                 | 0.45             | 52.3                 |
| 7   | 5.5                  | 500                         | 0.6                 | 0.45             | 46.9                 |
| 8   | 5.5                  | 550                         | 0.4                 | 0.65             | 66.4                 |
| 9   | 5.5                  | 600                         | 0.5                 | 0.25             | 58.9                 |

Table 5. Data processing results table.

| Factor | Calcination time (h) | Calcination temperature (℃) | Fe doping ratio (%) | N doping ratio (%) |
|--------|----------------------|-----------------------------|---------------------|------------------|
| K1     | 191                  | 165.9                       | 182.5               | 195.2            |
| K2     | 180                  | 225.4                       | 200.6               | 185.7            |
| K3     | 172.2                | 151.9                       | 160.1               | 162.3            |
| k1     | 63.67                | 55.3                        | 60.83               | 65.07            |
| k2     | 60                   | 75.13                       | 66.87               | 61.9             |
| k3     | 57.4                 | 50.63                       | 53.37               | 54.1             |
| R      | 6.27                 | 24.5                        | 13.5                | 7.97             |
3.2. Feasibility analysis of co-doping.

Benchmark test conditions: nitrobenzene wastewater samples from 2 L, concentration of 40 mg/L, pH value of 3, add 1 ml/L plus 30% oxidant H₂O₂, at 20 w UV lamp radiation under the conditions of photocatalytic reactor, add 10 g/L of photo catalyst, aeration (0.8 m³/ L), test reaction time is 3 h, every 30 min centrifugal nitrobenzene concentration sampling test. The activity was tested by comparing the nitrobenzene removal rate of water samples. Comparison of photo catalyst degradation with different doping conditions is shown in figure 2.

![Figure 2](image)

**Figure 2.** Effect of different doped photo catalyst on degradation of nitrobenzene wastewater.

According to the figure 3.2 shows that Fe, N doping TiO₂ / GF treatment effect is best, followed by Fe doped TiO₂ / GF, then the N doped TiO₂ / GF, the degradation of pure TiO₂ / GF rate is only 15.8%, lowest, metal and nonmetal doping more effectively improve the photocatalytic performance of the catalyst. The reason was that the N ion doping reduces the particle size of TiO₂ crystal at the same time expanding the surface area and Fe ion doping reduced TiO₂ light gave birth to the compound rate of electrons and holes, the synergy to maintain charge balance, restrain the formation of rutile phase, expanded the catalyst visible light response range, so as to improve its photocatalytic oxidation ability [13].

4. Conclusion

(1) Prepared by sol-gel method in the Fe,N photo catalyst doped TiO₂/GF, through orthogonal test, the biggest influence calcination temperature on catalytic activity of catalysts, Fe doping, N doping and the effect of calcination time.

(2) The best preparation conditions as follows: 2.5 h calcination time, calcination temperature 550 ℃, Fe doping amount 0.5% (mass fraction) and N doping amount is 0.45% (mass fraction), deal with 40 mg/L of nitrobenzene degradation, nitrobenzene wastewater degradation rate was 86.5%.

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