

Preparation and Photocatalytic Activity of Fe³⁺ - doped TiO₂ Modified

Li Yafeng, Yu Jiahui, Zhao Yanhong

School of Municipal and Environmental Engineering, Shenyang Jianzhu University, Shenyang, Liaoning, China

E-mail:1367803895@qq.com

Abstract: Photocatalytic materials of TiO₂ / coarse silica gel microspheres were prepared by sol-gel impregnation method and doped with transition metal ions Fe³⁺ to form Fe³⁺ modified TiO₂ / coarse silica gel microspheres. The surface of the Fe modified photocatalytic materials were analyzed by XRD and surface scanning. Degradation of reactive dyes using X-3B dye wastewater water samples for validation tests. The results show that the photocatalytic activity of the photocatalytic material reaches the best when the Fe doping amount is 0.5%, and the most photocatalyst amount is 10g / L. The degradation rate of COD under this dosage was 72.32%. At the same time, according to the characterization analysis, it was found that Fe did not react with the photocatalytic material of TiO₂ / coarse silica microspheres in the reaction, Fe increased the defect structure of TiO₂ surface and promoted the formation of anatase, A red shift occurred and the corresponding range of the spectrum expanded toward the visible region. The results show that the doping of Fe affects the formation of TiO₂ crystals, but increases the photocatalytic efficiency of TiO₂.

Keywords: Fe - doped; TiO₂; photocatalytic coarse – grained; silica microspheres.

1. Introduction

In China's industrial wastewater, dye wastewater accounts for a large proportion of its high organic content, complex composition, deep color, water quality changes, it is recognized at home and abroad more difficult to deal with industrial wastewater [1]. Dye wastewater treatment methods are adsorption, flocculation, chemical methods, biological methods [2], but a single treatment is generally difficult to achieve the desired effect in the economic rationality of the treatment, the current use of biological oxidation method, but many the pass rate of less than 60% [3]. Due to the current poor biodegradability, high chroma and high COD concentration of dye wastewater, the photocatalytic activity of TiO₂ has entered the field of vision in recent years. The research on TiO₂ photocatalytic oxidation began in 1972 and Fujishima and Honda [4] Mid - light Radiation TiO₂Sustainable Redox Reaction of Water. In 1976, J.H.Carry [5] et al. Reported that under ultraviolet light irradiation, TiO₂with photocatalytic oxidation can dechlorinate PCB, a refractory organic compound. Photocatalysis as a method of treating water caused Wide attention. Numerous studies show [6-8] that TiO₂ photocatalytic oxidation has become a new pollution control technology at home and abroad. The outer layer of semiconductor materials (such as TiO₂) has a special electronic structure, that is, it has a deep valence band level [9], has a strong redox ability, under the conditions of light, the organic matter completely oxidized and decomposed into CO₂, H₂O and other non-toxic and harmless substances. In the early research [10], TiO₂ was often suspended directly in solution and photocatalyzed directly. The photocatalytic efficiency of this reaction was not high, and nano- TiO₂ suspended in water could cause secondary pollution to the water. And as the catalyst itself does not participate in the reaction, suspended directly in the water is not conducive to secondary recycling.

Based on the above problems, the authors prepared the supported TiO₂and Fe³⁺ - TiO₂ photocatalysts by using the porous silica microspheres (2 ~ 3cm) as the carrier, and solved the powdery TiO₂ Lost, difficult to recycle the shortcomings and maintain good photocatalytic activity. The structure of the catalyst was characterized by XRD and photocatalytic activity. The optimum experimental conditions for the degradation of dye wastewater were discussed.

2. Experimental part

2.1 Reagents and equipment

The main test reagents used in the following table 1. The main instruments used in the experiment are shown in Table 2.

Table 1. Experiment reagents

Serial number	Name	Level
1	30% H ₂ O ₂	Analytical purity
2	Tetra butyl titanate	Analytical purity
3	Potassium dichromate	Analytical purity
4	Acetylacetone	Analytical purity
5	Absolute ethanol	Analytical purity
6	Nitric acid	Analytical purity
7	Sulfuric acid	Analytical purity
8	FeNO ₃ ·9H ₂ O	Analytical purity
9	Silver nitrate	Analytical purity
10	Silver sulfate	Analytical purity

Table 2. Experiment reagents

Serial number	Name	Model
1	UV germicidal lamp	20w
2	UV-visible spectrophotometer	UV-9100
3	PH meter	HI 98127
4	Electric thermostat blast drying oven	DHG-9140A
5	Muffle furnace	HH-4
6	Electronic analytical balance	FA1004N
7	Magnetic stirrer	GSP-77-03
8	Gas Rotameter	LZ ^B _J 6
9	X-ray diffractometer	D/Max-III A
10	Electron microscope	CP62-JSM-6390LV

2.2 Transition metal ions doped Fe³⁺ doped TiO₂ photocatalyst preparation

2.2.1 Vector pretreatment

The coarse silica gel microspheres as a carrier, the coarse silica gel microspheres washed with distilled water several times, pH = 4 solution soak 24h, and then washed with distilled water to neutral, the silica gel was placed in a glass crucible and placed in the drying oven drying, adjusting the temperature 130 °C drying 2h, cooled and placed in a sealed bottle spare.

2.2.2 Preparation of sol-gel doped transition metal ions Fe³⁺ -TiO₂ sol

In this experiment, a supported TiO₂ photocatalyst was prepared by the sol-gel method [11]. With n-tetrabutyl titanate as a precursor, butyl titanate, absolute ethanol and acetylacetone were mixed at a volume ratio of 100: 200: 15 Thoroughly mixed to form a solution A; then distilled water, absolute ethanol and concentrated HNO₃ are mixed in a volume ratio of 10: 100: 3 to form a solution B while adding Fe (NO)₃ solutions with different concentrations in solution B, 2d / s Slowly dropped into the strongly stirred solution A, stirring was continued for 2h after the addition was completed to form a uniform transparent orange yellow TiO₂ solution, which was aged for 24h to form a titania sol containing Fe³⁺ use. The doping amount of transition metal ions Fe³⁺ is calculated according to the mole percent of Fe³⁺ and TiO₂. According to the different doping amount, titania sol containing different concentrations of Fe³⁺ was prepared.

2.2.3 Doped transition metal ions Fe³⁺ supported TiO₂ photocatalyst preparation process

The dried silica gel microspheres with the diameter of 2 ~ 3mm are soaked in the prepared TiO₂ sol for 30min and uniformly loaded, and then dried in an electric drying box at a temperature of 130 ° C for 2h On the muffle furnace calcined 2h. Preparation of coated TiO₂ film. Repeated impregnation, drying, calcination, coating films can be prepared by varying the number of doped transition metal ions Fe³⁺ TiO₂ film. That is doped with transition metal ions Fe³⁺ supported TiO₂ photocatalyst. The specific process is shown in Figure 1.

2.3 Photocatalytic degradation

The photocatalytic reaction was carried out in a self-made reactor. The bottom of the reactor was equipped with a ring-type aerator. The effective volume of the reactor was 2.6L and the reactive brilliant red X-3B dye wastewater of 50mg / L (COD 100mg / L) The membrane was added into the reactor 5 times, after calcined at 450 °C for 2h, the supported Fe³⁺ -TiO₂ photocatalyst 10g / L was aerated to make it suspend. The reaction was proceeded under the irradiation of UV lamp. The initial concentration of degradation was 50mg / L, COD100mg / L of reactive brilliant red dye wastewater, adjusting the solution pH value 3, the aeration rate of 0.6m³/L, adding 3% H₂O₂ 0.6ml/L, sampling interval for a period of time for analysis, the maximum absorption the wavelength of 540nm at the absorbance, can be calculated under different reaction conditions dye degradation and COD removal rate.

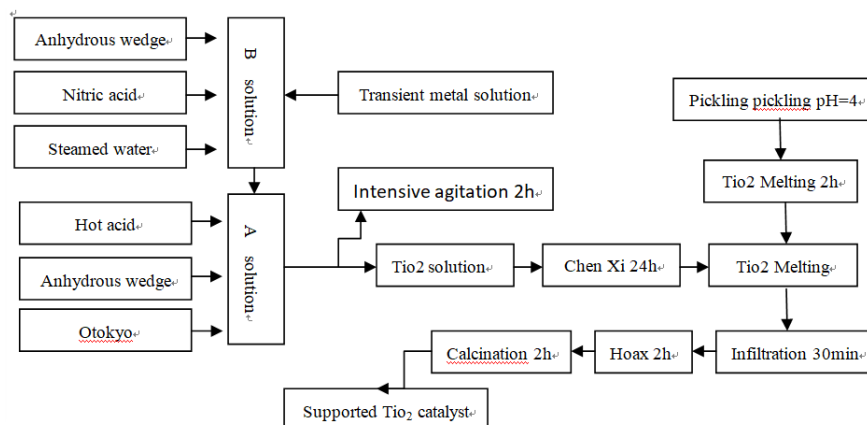


Fig 1. The preparation of the immobilized Fe^{3+} - TiO_2 activator preparation technological process

3 Results and discussion

3.1 Supported Fe^{3+} - TiO_2 surface macro performance

During the experiment, in order to facilitate the observation of the change of the surface of the support, the supported photocatalyst doped with Fe^{3+} and pure TiO_2 after 450°C was scanned under an electron microscope at 160 times as shown in FIG. 2 (a- TiO_2 b- Fe^{3+} - TiO_2). As can be seen from the figure, the surface of the Fe^{3+} - TiO_2 catalyst crystallizes better and the color of the surface changes. It is preliminarily determined that iron oxide may enter the crystal lattice of TiO_2 and there is no TiO_2 anatase phase structure.

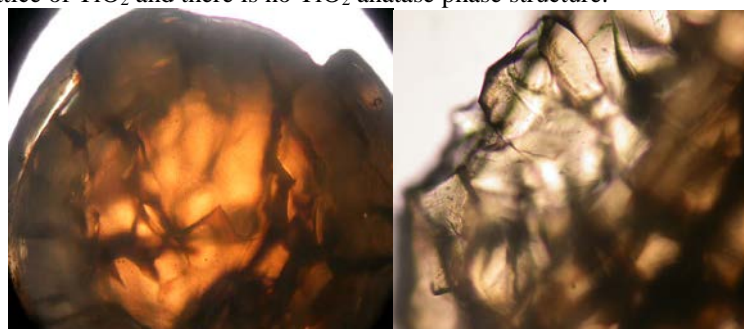


Fig 2. The contrast pictures of the Immobilized TiO_2 and Fe^{3+} - TiO_2 activator macroscopical surface structure (a- TiO_2 , b- Fe^{3+} - TiO_2)

3.2 Fe^{3+} - TiO_2 XRD characterization

From the results of XRD test in Fig. 3 (a, b), it can be seen that both anatase TiO_2 and Fe^{3+} - TiO_2 are calcined at 450°C for 2h (the highest peak corresponds to 2θ in the range of $24.7 \sim 26.3^\circ$), Fe^{3+} Of the TiO_2 crystal structure does not change, by XRD analysis did not find the formation of iron oxide, such as Fe_2O_3 or Fe_3O_4 crystal phase (diffraction peak corresponding to 2θ does not exactly correspond), Fe^{3+} doping, peak sharpening, intensity Enhanced. The reason is that the distribution of iron in the TiO_2 film increases the defect structure of the TiO_2 surface, which makes the surface electrons different in energy from the band structure of TiO_2 main body [12], which promotes the formation of anatase and absorbs the edge of absorption band the red shift, doped Fe^{3+} doped TiO_2 photocatalyst spectral range corresponding to the visible region of expansion in the XRD spectrum showed anatase diffraction peak enhanced.

When the doping amount is 0.5% (mole fraction), no diffraction peak of iron species is observed. Only the diffraction peak near Fe_2O_3 appears, which may be due to the low doping amount of iron into the TiO_2 lattice or the high dispersion of Fe_2O_3 on the surface of TiO_2 [13], Fe_2O_3 grains are too small to go beyond the technical scope of XRD, so the existence of Fe_2O_3 can not be detected. However, it can be seen from Fig 3 that if the doped Fe^{3+} is too high, an excessive amount of Fe_2O_3 will cover the surface of the TiO_2 to reduce its photocatalytic activity.

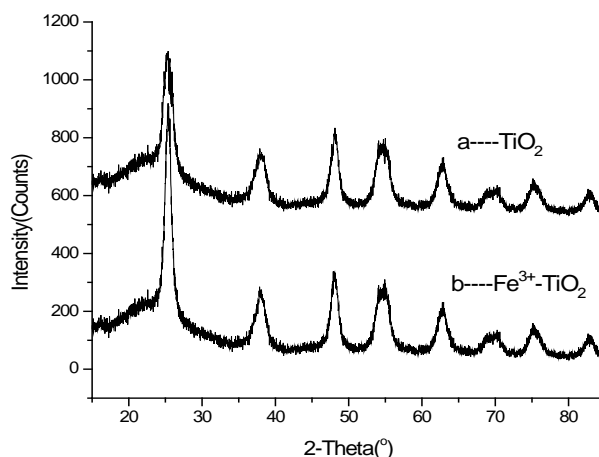


Fig 3. The XRD patterns of TiO_2 (a) and $\text{Fe}^{3+}\text{-TiO}_2$ (b) particles (450°C)

3.3 Metal ions Fe^{3+} doping on the activity of $\text{Fe}^{3+}\text{-TiO}_2$ photocatalyst

Take 2.6L 50mg / L of reactive brilliant red X-3B dye wastewater samples, adjust the wastewater pH = 3, placed in a photocatalytic reactor, the introduction of air ($0.6\text{m}^3 / \text{L}$) to make the supported catalyst in suspension, respectively, Doped $\text{Fe}^{3+}\text{-TiO}_2$ photocatalyst with Fe^{3+} doping amount (molar percentage) of 0, 0.05%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7% and 0.8% 10g / L, the reaction was carried out in 20W UV lamp 2h. According to the removal of dye color and COD removal rate, the photocatalytic activity of $\text{Fe}^{3+}\text{-TiO}_2$ catalyst with different Fe^{3+} doping amount was judged and compared. The test results are shown in Figure 4.

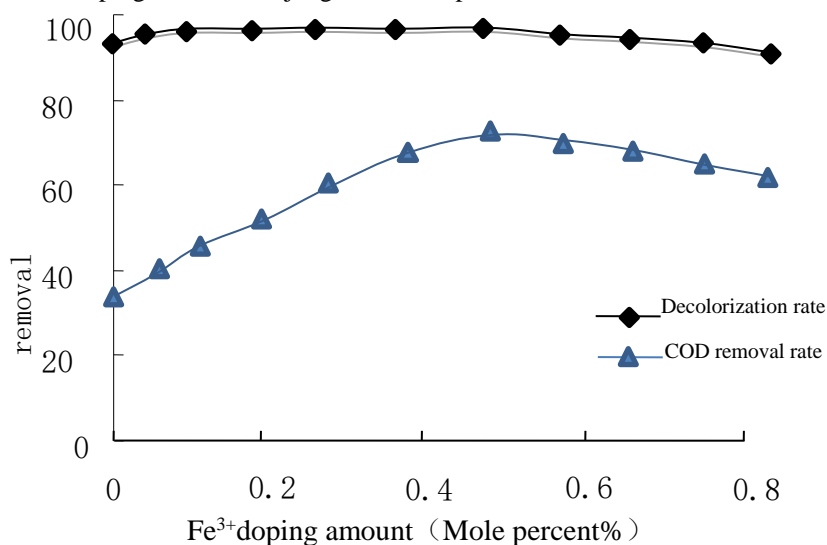


Fig 4. The effect of intermixing Fe^{3+} on the Immobilized $\text{Fe}^{3+}\text{-TiO}_2$ photo catalytic activity

The experimental results show that compared with non-doped $\text{Fe}^{3+}\text{-TiO}_2$ photocatalyst, $\text{Fe}^{3+}\text{-TiO}_2$ photocatalyst significantly enhances the photocatalytic activity of TiO_2 , promotes the interfacial reaction of hole transport, and the amount of doping has a significant effect on the catalytic performance. An optimal value. The specific performance of the reaction at 2h, with the increase of Fe^{3+} doping $\text{Fe}^{3+}\text{-TiO}_2$ photocatalytic degradation of dye wastewater color removal rate is not significant, but the removal rate of COD showed a significant increase first and then decrease, and at the doping amount of 0.5%, the removal rates of chroma and COD reach the highest points of 99.98% and 72.32% respectively at the same time. From a chemical point of view, Fe^{3+} as an effective electron acceptor can capture electrons. Due to the scramble of metal ions for electrons, Fe^{3+} can reduce the electron-hole recombination probability of the TiO_2 surface, resulting in more oxidized $\cdot\text{OH}$, increased catalyst activity. In addition to the photocatalytic reaction of TiO_2 in the system, there may be the following reaction [14]:





It can be seen from (1),(2),(3)and (4) -that the doped Fe^{3+} can absorb electrons and inhibit hole-electron recombination. On the other hand, Fe^{2+} With the role of H_2O_2 , can generate $\cdot\text{OH}$, $\cdot\text{OH}$ is a strong oxidant, can oxidize a variety of reactive dyes.

3.4 Calcination temperature on Fe^{3+} - TiO_2 photocatalytic activity

Take 2.6L50mg / L (COD of 100mg / L) of reactive Brilliant X-3B dye wastewater samples, adjust the wastewater pH = 3, placed in a photocatalytic reactor, the introduction of air (0.6m^3 / L) The photocatalyst is in suspension state, and the doped Fe^{3+} - TiO_2 photocatalyst 10g / L, which is made by calcination temperature 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 2h respectively, The amount was 0.5% (mole%) and the reaction was allowed to proceed for 2h under irradiation with a 20W UV lamp. The photocatalytic activity of the catalyst at each calcination temperature was judged and compared according to the removal of the dye color and the COD removal rate. The test results are shown in Figure 5.

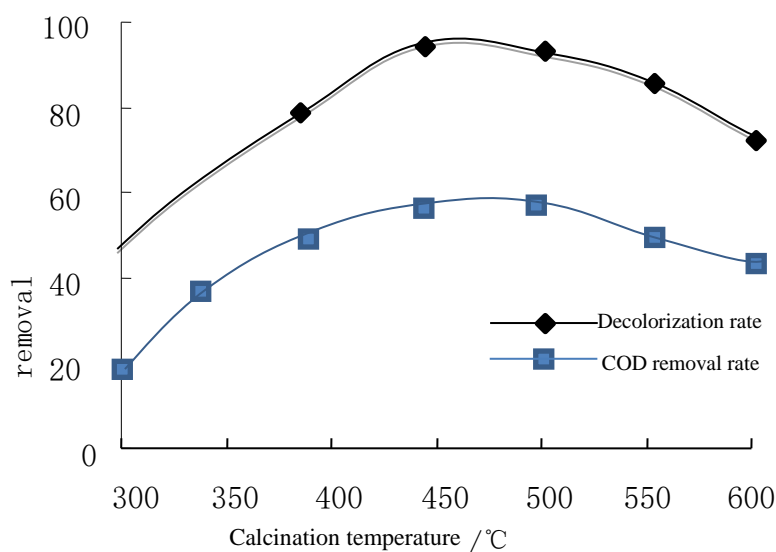


Fig 5. The effect of calcined temperature on the Immobilized Fe^{3+} - TiO_2 photo catalytic activity

The results show that under the same conditions, the decolorization rate and COD removal rate of the azo dye reactive brilliant red X-3B are the lowest when the calcination temperature is 300 °C, and the decolorization rate and COD removal rate are both high at 450 °C ~ 500 °C. At 450 °C reached the highest chroma and COD removal rates were 99% and 75%, respectively, and then with the calcination temperature decreased removal rate decreased. The reason may be that at 300 °C, the vast majority of catalysts are still amorphous or anatase structure, and anatase structure is not obvious [15]. Anatase accounts for the vast majority after 450 °C ~ 500 °C, and with the increase of temperature, the anatase gradually transformed into rutile type. The calcination temperature of the catalyst doped with Fe^{3+} was 450 °C.

3.5 Calcination time on Fe^{3+} - TiO_2 photocatalytic activity

The calcination time has the same effect on the activity of Fe^{3+} - TiO_2 photocatalyst as calcination temperature. Take 2.6L50mg / L Reactive Brilliant X-3B dye wastewater sample water, adjust the wastewater pH = 3, placed in a photocatalytic reactor, the introduction of air (0.6m^3 / L) so that the supported catalyst is in suspension, respectively calcined the doped Fe^{3+} - TiO_2 photocatalyst 10g / L was prepared at a constant temperature of 450 °C for 0h, 1h, 1.5h, 2h, 2.5h, 3h, 3.5h and 4h. The doping amount was 0.5% (mol% The reaction was carried out for 2h with irradiation of 20W UV lamp. The photocatalytic activity of the catalyst under each calcination time was judged and compared according to the removal of the dye color and the COD removal rate. The test results are shown in Figure 6.

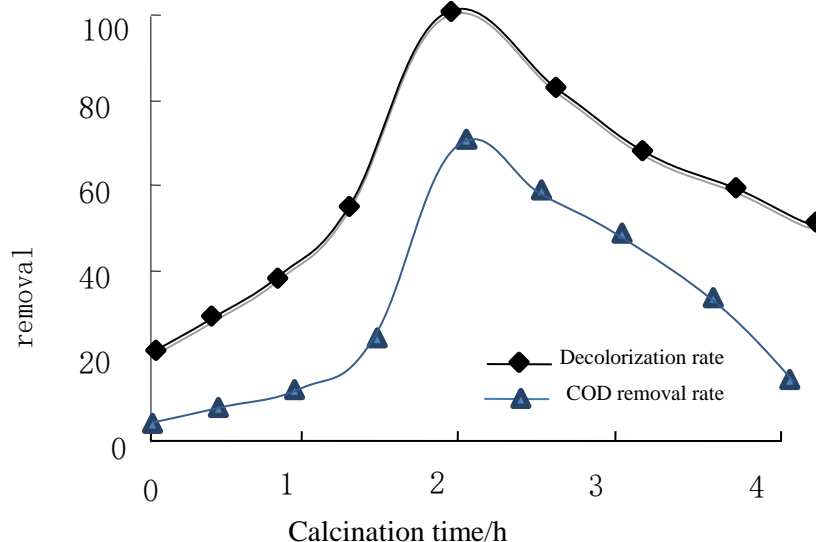


Fig 6. The effect of calcination time on the Immobilized Fe^{3+} - TiO_2 photo catalytic activity

The experimental results show that under the same conditions, with the different calcination time of Fe^{3+} - TiO_2 photocatalyst at 450°C , the chromaticity and COD removal rate of Reactive Brilliant Red X-3B dye dyestuff obviously increase first and then decrease. With the calcination time of the photocatalytic activity is getting better and better, at 2h the best photocatalytic activity of colorimetric and COD removal were 99%, 70%, then the longer the constant temperature chroma and COD decreased rapidly, because the catalyst After the precursor is calcined at high temperature, no active crystalline phase has been formed for a short time [16]. Due to the relatively slow growth of the crystal, sufficient time is required to form the active crystalline phase. However, calcination time is too long will cause the catalyst grain growth, so that the surface activity decreased, decreased photocatalytic activity, and thus determine the calcination time of 2.0h is appropriate. This point is consistent with the pure TiO_2 photocatalyst Fe^{3+} - TiO_2 photocatalyst, indicating that the doping metal ions Fe^{3+} TiO_2 at 450°C constant time 2.0h crystal phase did not change, but the doping Fe^{3+} caused TiO_2 lattice defects, inhibited Electron - hole compound, so that its photocatalytic activity than pure TiO_2 photocatalytic activity much higher.

3.6 Comparison of Photocatalytic Activity of Fe^{3+} - TiO_2 with Pure TiO_2

Under the same experimental conditions, a comparison experiment was made between the catalyst doped with Fe^{3+} (5%) and the pure catalyst. The calcination temperature was 450°C , the number of plating was 5 times, the calcination time was 2h, and the activity of COD was 100mg / L Brilliant X-3B dye wastewater 2.6L, pH = 3, aeration 0.6m³ / h, control the reaction time 2h, and samples taken at intervals of time for experimental analysis. The test results are shown in Figure 7 and 8.

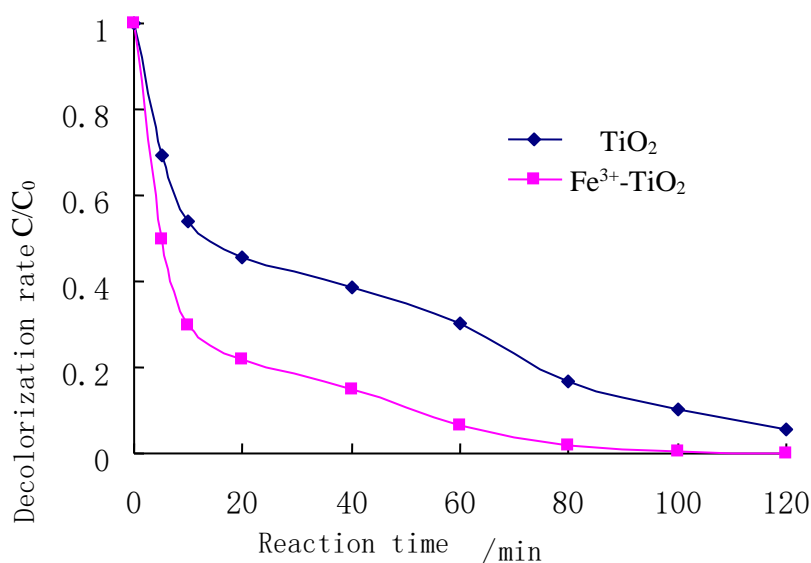


Fig 7. The photo catalytic chroma degradate velocity contrast on the Reactive brilliant red X-3B wastewater between the TiO_2 and Fe^{3+} - TiO_2

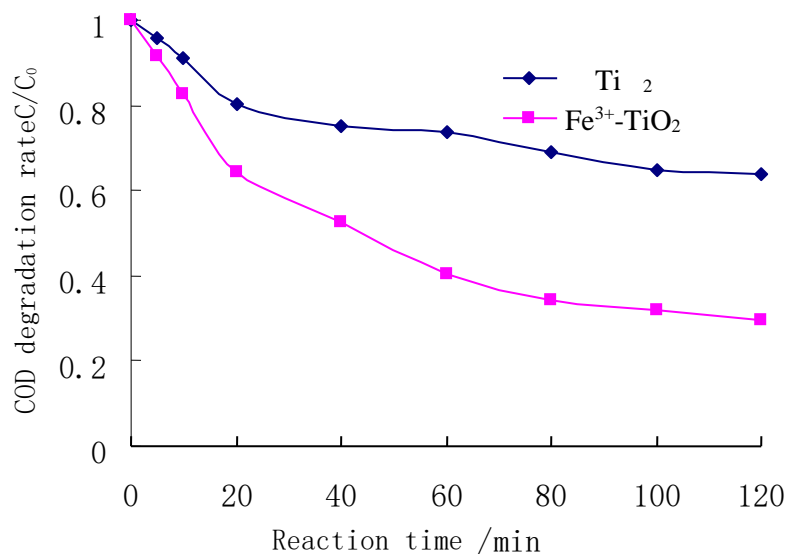


Fig 8. The photo catalytic COD degradatevelocitycontrast on the Reactive brilliant red X-3B wastewater between the TiO₂ and Fe³⁺-TiO₂

The experimental results show that the photocatalyst doped with Fe³⁺ -TiO₂ degrades dye wastewater much faster than the pure TiO₂ photocatalyst, especially in the COD removal has been greatly improved, mainly due to [17] doped in TiO₂ Fe³⁺, the catalyst properties change, Fe³⁺ doping may introduce defects in the TiO₂ lattice position or change the degree of crystallinity into a trap of electrons or holes to extend the life not only can enhance the photocatalytic TiO₂ effect, it is also possible to The absorption wavelength of TiO₂ extends to the visible region. In addition, during the purification of doped samples, the specific surface area of Fe³⁺ -TiO₂ is smaller than that of pure TiO₂ at the same calcination temperature, and the phase transition of TiO₂ from anatase to rutile can be suppressed [18] and the anatase phase of TiO₂ Photocatalytic activity than rutile phase, which is also incorporation of Fe³⁺ TiO₂ than pure TiO₂ film activity is another important reason. Therefore, the doping of Fe³⁺ increases the photocatalytic activity of the catalyst and accelerates the photocatalytic reaction.

4 Conclusion

(1) n-Tetrabutyl titanate was used as precursor, anhydrous ethanol was used as catalyst solvent and coarse-grained silica microspheres was used as carrier. The supported TiO₂ photocatalyst was prepared by sol-gel method. When Fe³⁺ doping amount was 0.5 %, The calcination temperature is 450 °C, incubated for 2.0h, the coating layer number is 5, the photocatalytic activity is the best.

(2) Through the influence of TiO₂ and Fe³⁺ -TiO₂ on the degradation rate of reactive brilliant red X-3B, the photocatalytic activity of Fe³⁺ -TiO₂ photocatalyst is higher than that of TiO₂.

(3) In the same time, the photocatalytic degradation of dye wastewater with Fe³⁺ -TiO₂ is more effective than that of the photocatalytic degradation of dye wastewater with removal of chrominance and removal of COD. The reaction rate is increased and the reaction time is shortened. However, Mature, currently only used in the laboratory research stage, so the preparation of efficient and cheap supported Fe³⁺ -TiO₂ photocatalyst will certainly become the hot spot, so that it can be better applied to the actual biodegradable wastewater treatment.

5 References

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