

Photocatalytic Degradation of NH₃-N in Aquaculture Wastewater by Using CaF₂(Tm³⁺)/TiO₂ under UV Light

Z W Nie, X C Yu*, J H Liu, L P Wang and M C Guo

College of Ocean Technique and Environment department, Dalian Ocean University, China

Corresponding author and e-mail: X C Yu, xiaocyu@dlou.edu.cn

Abstract. The TiO₂ doped with CaF₂(Tm³⁺) photocatalyst is employed to degrade NH₃-N in aquaculture wastewater under UV light. The photocatalyst was prepared by Sol-gel method and characterized by SEM, EDS and XRD analysis. The effects of doping ratio of CaF₂(Tm³⁺), dosage, initial concentration of NH₃-N, pH value, concentration of H₂O₂ and illumination time on NH₃-N removal were investigated. The optimal conditions for the degradation of NH₃-N were as follows: the catalyst doping ratio was 15%, the dosage was 0.2 g/L, the initial concentration of ammonia nitrogen was 80 mg/L, the concentration of hydrogen peroxide was 0.3 g/L, the pH value was 10 and the UV light irradiation time was 3 h. In this case, the removal rate of NH₃-N can reach 68.34%. The results show that CaF₂(Tm³⁺)/TiO₂ photocatalyst can effectively remove NH₃-N in aquaculture wastewater under UV light.

1. Introduction

In recent years, aquaculture industry has been developing rapidly with the development of economy. Meanwhile, water environment has been seriously affected by the direct discharge of untreated aquaculture wastewater[1]. As a main target pollutant in aquaculture wastewater, NH₃-N can cause the explosion of eutrophication in a large area. The eutrophication not only seriously deteriorates the water quality, but also leads to large-scale reproduction of algae and excessive consumption of oxygen in the water, which leads to a severe hypoxic environment of the water. Fish is poisoned by breeding pests, endangering human health[2]. Therefore, the treatment of NH₃-N is extremely urgent.

Zhang W[3] used ZnO series as catalysts to treat NH₃-N wastewater. The results showed that the removal rate of NH₃-N can reach 66%. Compared with ZnO, TiO₂ has been widely studied in recent years, for corrosion resistance, no secondary pollutant, low expense and other characteristics. In particular, the strong catalytic oxidation capacity of TiO₂ makes it widely applied in environmental pollution control[4]. TiO₂ is a wide bandgap semiconductor which can only absorb near UV light. Nowadays, people have been using precious semiconductor composite, metal deposition and other methods to modify TiO₂ to improve the spectral absorption range of TiO₂[5]. Many studies have shown that the final product of photocatalytic degradation of NH₃-N is N₂[6]. In this study, a TiO₂ doped CaF₂(Tm³⁺) photocatalyst is employed to degrade NH₃-N in aquaculture wastewater under UV light.

2. Experimental

2.1. Materials

The main chemicals include $(\text{NH}_4)_2\text{SO}_4$, phenol, NaClO, Sodium citrate, Tm_2O_3 , HF, CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$, tetrabutyl titanate(TBOT), $\text{Ca}(\text{NO}_3)_2$, HNO_3 and H_2O_2 .

2.2. Preparation of $\text{CaF}_2(\text{Tm}^{3+})$ nanoparticles

$\text{CaF}_2(\text{Tm}^{3+})$ nanoparticles were prepared by co-precipitation method. In a typical experiment, a saturated solution of $\text{Ca}(\text{NO}_3)_2$ was prepared using deionized water as a solvent. Under heating conditions, a prescribed amount of Tm_2O_3 was dissolved in concentrated HNO_3 . Then, under the condition of stirring, $\text{Ca}(\text{NO}_3)_2$ solution and $\text{Tm}(\text{NO}_3)_3$ respectively drops into the HF solution at a certain rate ($\text{Ca}^{2+}:\text{F}^- = 1:2$, $\text{Tm}^{3+}:\text{F}^- = 1:3$; molar ratio), after the titration, the magnetic stirring was continued for 1 h. After this, the solution was centrifuged and washed 6 times to remove the remaining NO_3^- . After drying and grinding, the $\text{CaF}_2(\text{Tm}^{3+})$ nanoparticles was obtained.

2.3. Preparation of $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ photocatalyst

$\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ photocatalyst was synthesized using sol-gel method. TBOT, ethanol and a small amount of glacial acetic acid were mixed and vigorously stirred to form solution A. The precise amount of $\text{CaF}_2(\text{Tm}^{3+})$ nanoparticles was dissolved in deionized water and an appropriate amount of ethanol was added. After 15 min of ultrasonic separation, solution B was obtained. Under the condition of stirring, solution B was added dropwise to solution A. After the titration, the stirring was continued for 60 min. After standing for 24 h, the sol was dried at $80\text{ }^\circ\text{C}$ for 12 h and ground to powder, then the powder was calcined at $450\text{ }^\circ\text{C}$ for 2 h. Then, the samples were ground to form $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ photocatalyst. The molar ratios of Tm^{3+} to TiO_2 are 0, 5, 10, 15, 20 and 25%.

2.4. Characterization techniques

The crystal structures of all prepared samples were characterized by X-ray diffraction (XRD) using a D/MAX-2500X ray diffractometer with $\text{Cu K}\alpha$ radiation (Japan). Scanning electron microscopy (SEM) images using a Quanta 200FEG field emission environment scanning electron microscopy (American) were employed to obtain a variety of physical and chemical properties of prepared samples, such as morphology, composition, crystal structure, etc.

2.5. Photocatalytic activity measurements.

The photocatalytic activity of the $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ photocatalyst under UV light(intensity: 18W) was evaluated by measuring degradation of $\text{NH}_3\text{-N}$ in aquaculture wastewater. According to the experimental requirements, different amounts of $(\text{NH}_4)_2\text{SO}_4$ were added in the seawater after pumping (sampled in the waters near Dalian Ocean University, ammonia concentration of 0.9725 mg/L, pH=7.98) to obtain simulated aquaculture wastewater. The photocatalytic degradation of $\text{NH}_3\text{-N}$ was analysed by various experimental parameters namely doping ratio, dosage, initial concentration of $\text{NH}_3\text{-N}$, pH value, concentration of H_2O_2 and illumination time. The content of $\text{NH}_3\text{-N}$ was estimated by indophenol blue colorimetric method[7].

3. Results and discussion

3.1. The characterization of $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ photocatalyst

The XRD patterns of materials are shown in Figure 1. TiO_2 has obvious peaks at 2θ of 25.4287° , 37.8204° , 47.9708° and 70.3778° . The $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ with doping ratio of 15% has obvious peaks when 2θ is 25.3284° , 28.0843° , 38.0536° and 55.2359° . The photocatalyst of 25% has obvious peaks at 2θ of 25.3289° , 28.0858° , 37.9646° and 55.1043° . Scherrer formula was used to calculate the

average particle size of the prepared photocatalyst. The lattice constants a, b and c of TiO₂ are 3.7830, 3.7839 and 9.5100 Å; the lattice constants a, b and c of 15% are 3.7852, 3.7852 and 9.5139 Å and 25% are 6.2782, 6.8131 and 4.4097 Å. The average crystallite sizes of TiO₂, photocatalyst with the doping ratio of 15, 25% are 17.72, 15.51 and 20.67 nm, respectively. The diffraction peak positions of the materials coincide well with those of the TiO₂ standard (JCPDS No. 89-4921).

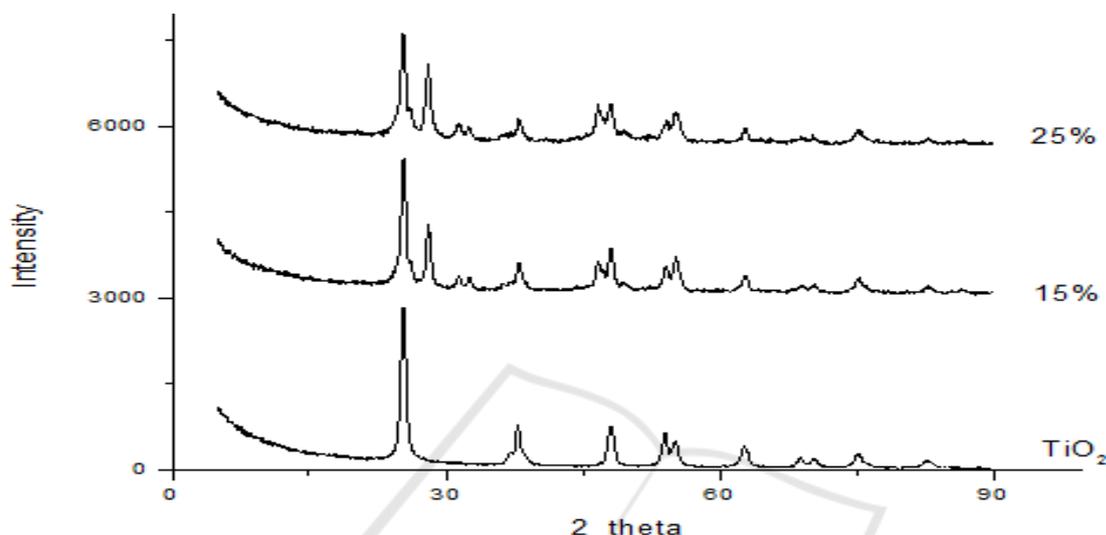


Figure 1. XRD pattern of CaF₂(Tm³⁺)/TiO₂ photocatalyst with different doping ratios.

The typical SEM images are shown in Figure 2 (magnification 100 k times). The doping ratios of a, b are 0 and 15% respectively. It can be seen from the figure that the TiO₂ particles display a regular globular structure. Compared with pure TiO₂, larger particles appear in (b). It can be deduced that the particle size of CaF₂(Tm³⁺) is larger than that of TiO₂. Besides, compared with Figure 2a, Figure 2b shows a better crystallinity.

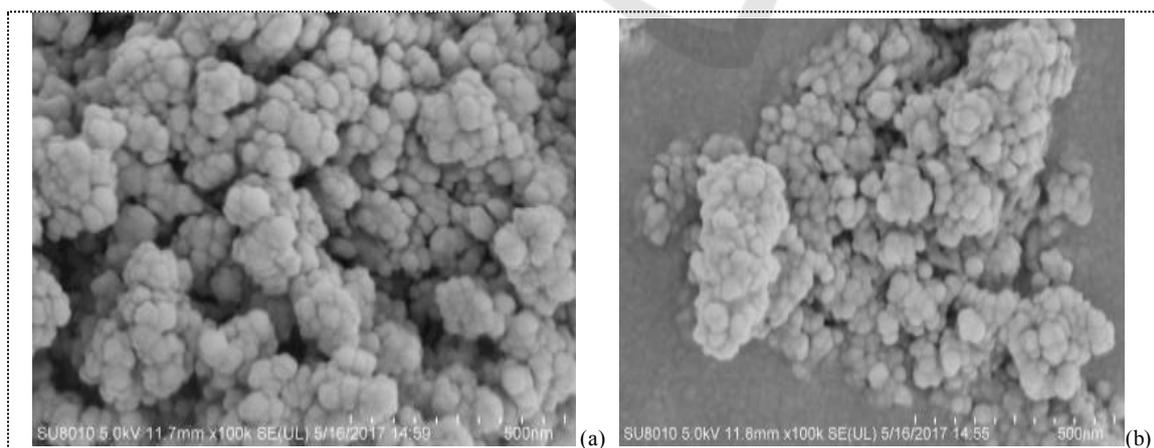


Figure 2. SEM images of CaF₂(Tm³⁺)/TiO₂ photocatalysts with different doping ratios.

In order to further determine the presence and relative content of Tm in CaF₂(Tm³⁺)/TiO₂, the sample was characterized by EDS. The EDS spectrum of the sample is given in Figure 3. From the

figure, the sample contains Ti, O, and Tm, Ca, F, their contents are listed in the illustration. This proves that $\text{CaF}_2(\text{Tm}^{3+})$ has been well doped in TiO_2 .

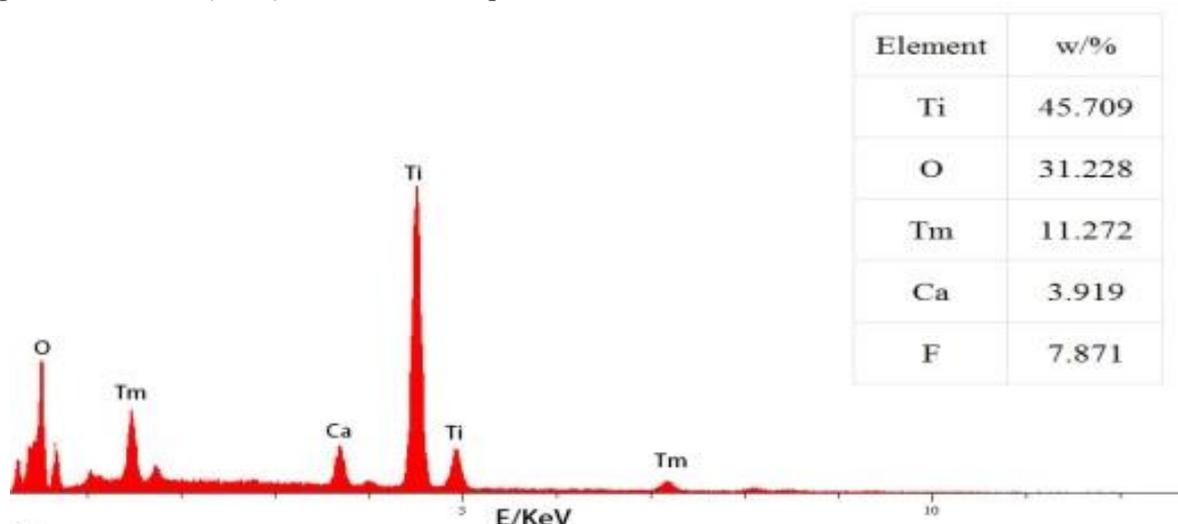


Figure 3. EDS images of $\text{CaF}_2(\text{Tm}^{3+}) / \text{TiO}_2$.

3.2. The effect of doping ratio on photocatalytic reaction

The concentration of $\text{NH}_3\text{-N}$ was controlled at 100 mg/L; the pH value of aquaculture wastewater was 8.0; the dosage of photocatalyst was 0.6g/L; the concentration of H_2O_2 was 0.3g/L; the illumination time was 2.0 h and the doping ratio of $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ was 0, 5, 10, 15, 20, 25 % . The rate of degradation could be calculated after the reaction.

The results shown in Figure 4 (a), the removal rate increased with the increase of doping ratio, reached the maximum at 15%, and then the removal rate began to decrease. The possible reason is that when the doping ratio is more than 15%, TiO_2 is covered with excess upconversion material, which makes the photocatalytic activity of TiO_2 decrease, so the removal rate decreases gradually.

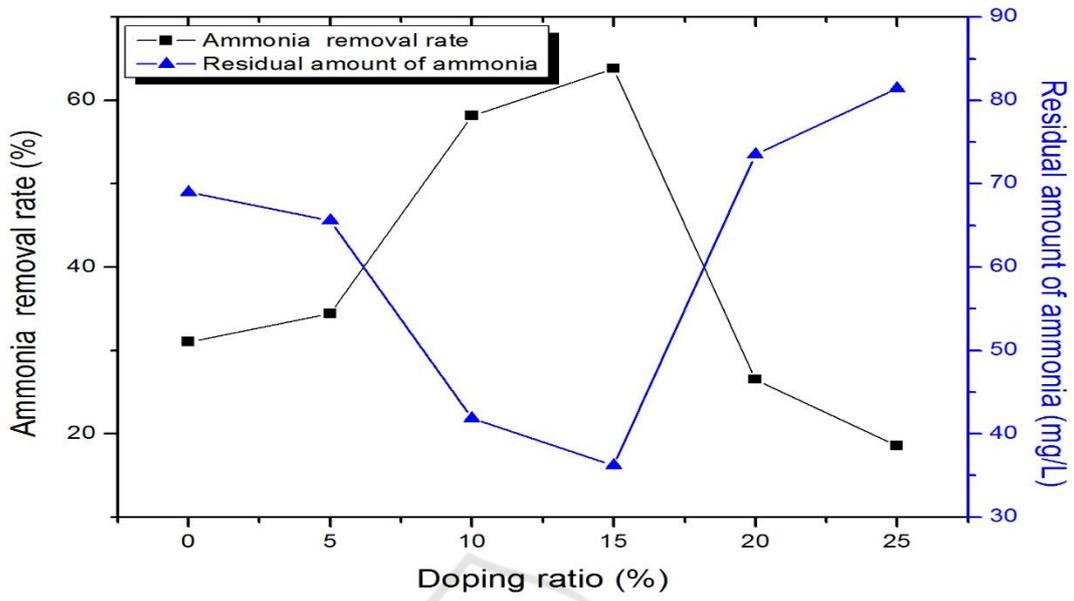
3.3. The effect of dosage on photocatalytic reaction

The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15% and the dosage were 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 g/L.

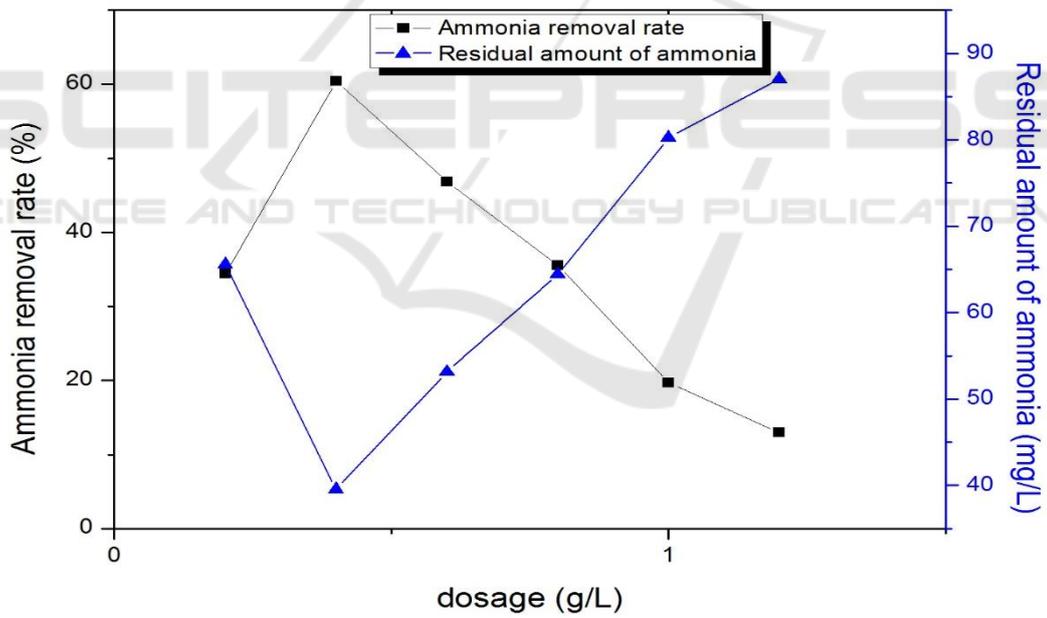
As shown in Figure 4(b), as the dosage increases, the removal increases first and then decreases. The maximum is 60.43% at 0.4 g/L. At the beginning, the removal rate is gradually increased due to the more catalyst involved in the reaction, so that the reaction is carried out more completely. When the dosage is more than 0.6 g/L, the removal rate decreases with the increase of catalyst dosage, which is mainly due to the scattering of light[8].

3.4. The effect of initial concentration of $\text{NH}_3\text{-N}$ on photocatalytic reaction

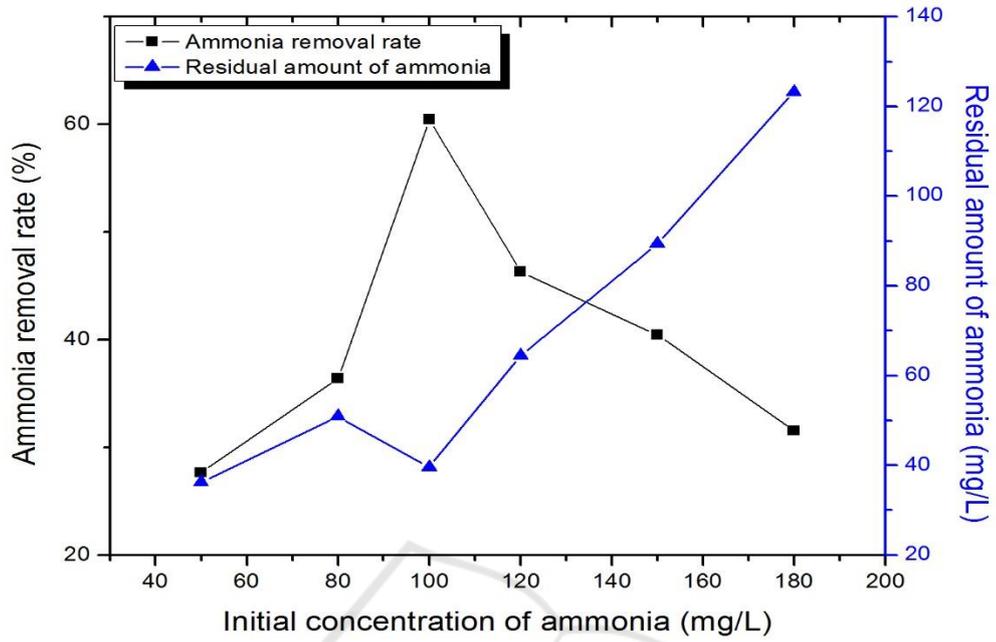
The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15%, the concentration of $\text{NH}_3\text{-N}$ were 50, 80, 100, 120, 150 and 180 mg/L.



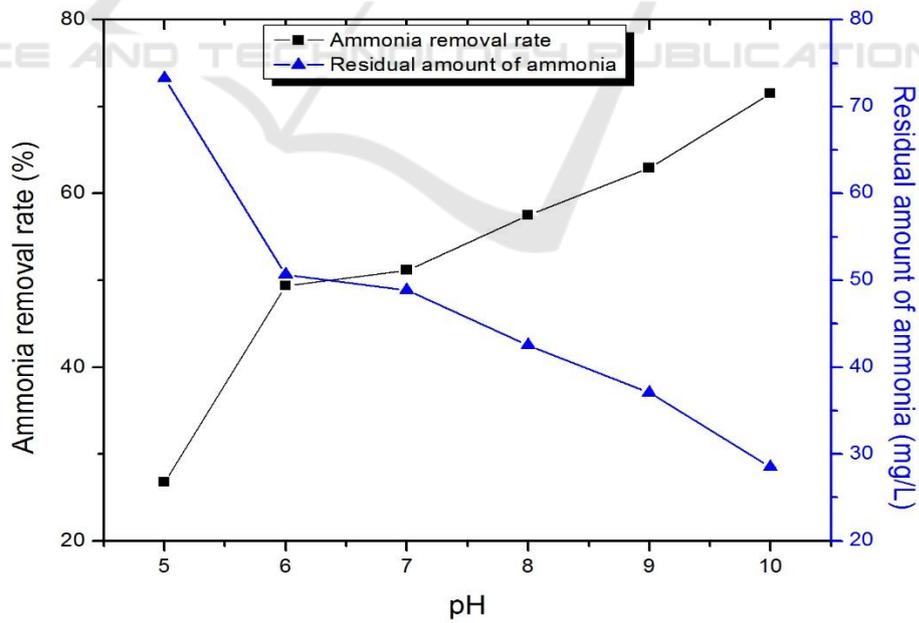
(a)



(b)



(c)



(d)

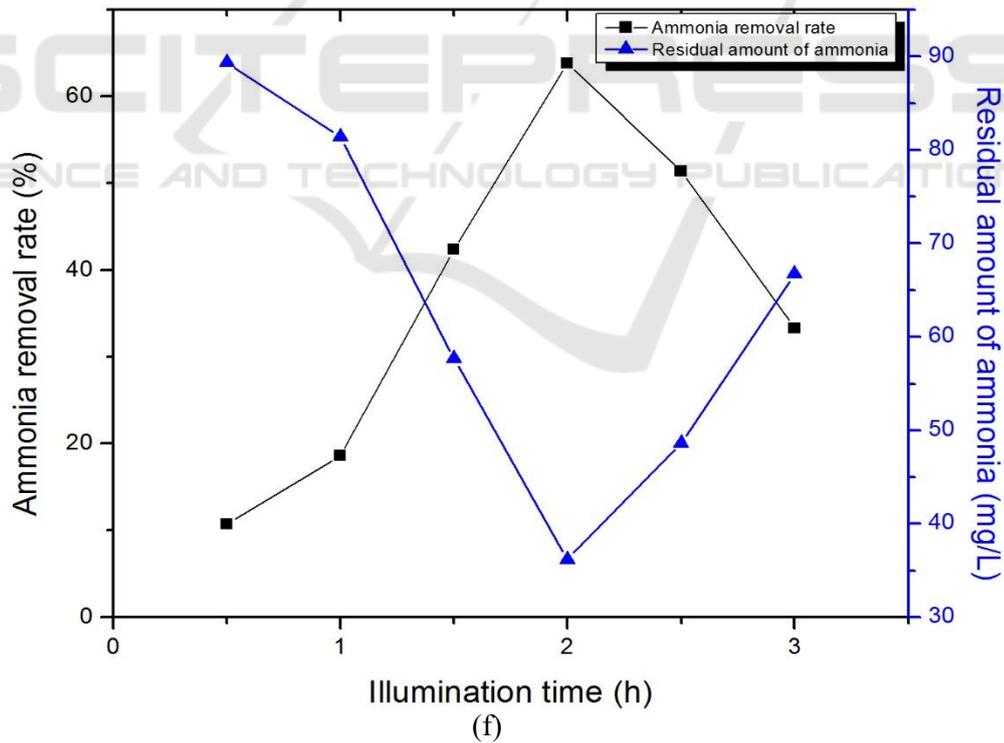
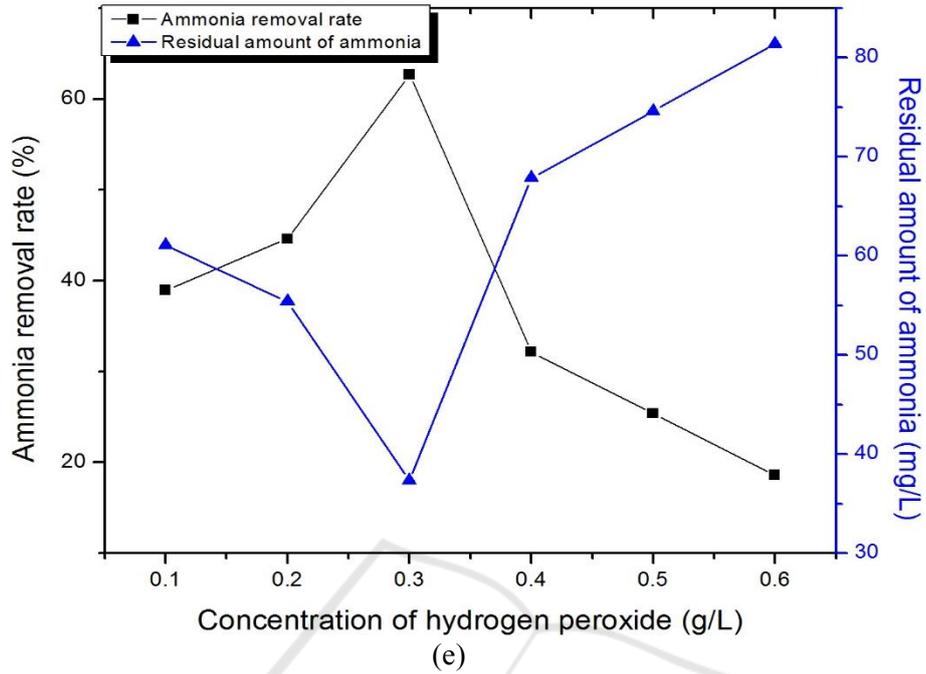


Figure 4. Effect of doping ratios of CaF₂(Tm³⁺)/TiO₂(a), dosage (b), initial concentration of NH₃-N (c), pH (d), concentration of hydrogen peroxide(e), illumination time (f) on ammonia nitrogen removal rate.

The results show in Figure 4(c), it is clear that when the initial concentration of $\text{NH}_3\text{-N}$ is 100 mg/L, the removal rate can reach 60.43%. The low initial concentration of $\text{NH}_3\text{-N}$ has influence on the reaction of photocatalytic process due to the generation of photo-generated electron-hole pairs is suppressed, which leads to the effects on removal of $\text{NH}_3\text{-N}$ directly. However, the initial concentration of $\text{NH}_3\text{-N}$ reaches a certain value, a large number of pollutants will be attached to the catalyst surface and the catalyst can not be completely contacted with contaminants. Thus, moderate concentration of $\text{NH}_3\text{-N}$ will increase the removal rate.

3.5. The effect of pH value of aquaculture wastewater on photocatalytic reaction

The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15%, pH value of aquaculture wastewater were 5, 6, 7, 8, 9 and 10.

It can be seen from Figure 4(d) that the removal rate gradually increases with the increase of pH and reach 71.51% at pH of 10. The $\text{NH}_3\text{-N}$ in the wastewater essentially exists in equilibrium in the form of NH_4^+ and NH_3 . With the increase of pH, the number of $\cdot\text{OH}$ will increase so the removal rate of $\text{NH}_3\text{-N}$ will increase. Meanwhile, with the increase of pH, a part of the NH_3 molecules will be blown out of the air in the mixing process[9]. Therefore, the higher the pH, the better the removal of $\text{NH}_3\text{-N}$.

3.6. The effect of concentration of H_2O_2 on photocatalytic reaction

The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15%, concentration of H_2O_2 were 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g/L.

It can be seen from Figure 4(e) that the maximum removal rate is obtained when the concentration of H_2O_2 is 0.3 g/L. Related studies[10] have shown that H_2O_2 can promote photocatalytic degradation. As a strong oxidant, H_2O_2 will produce a photo-generated electrons capture and result in photo-generated electrons and hole separation[11]. However, H_2O_2 is also used as a scavenger for the formation of $\cdot\text{OH}$ and $\cdot\text{O}^{2-}$. Thus, both a small and excess amount of H_2O_2 will inhibit the reaction.

3.7. The effect of illumination time on photocatalytic reaction

The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15%, illumination time were 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 h.

The results are shown in Figure 4(f). With the increase of time, the removal rate increases first and then decreases and the best removal rate can reach 63.82% at 2.0 h. The presence of oxygen molecules in the water can continuously capture the photo-generated electrons, which results in an increase in $\cdot\text{OH}$ and $\cdot\text{O}^{2-}$, which can improve the efficiency of photocatalytic degradation of $\text{NH}_3\text{-N}$ [12].

3.8. The optimization of photocatalytic conditions of $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$

The photocatalytic degradation of $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$ was analysed by different experimental parameters namely doping ratio, dosage, initial concentration of $\text{NH}_3\text{-N}$, pH value, concentration of H_2O_2 and illumination time. Here, six factors and five levels table was designed and the results of the orthogonal test are shown in Table 1.

Table 1. The results of the orthogonal test.

Experiment	Time/(h)	Initial concentration of NH ₃ -N/(mg·L ⁻¹)	Doping ratio/(%)	Dosage/(g·L ⁻¹)	Concentration of H ₂ O ₂ / (g·L ⁻¹)	p H value	Ammonia nitrogen removal rate / (%)
1	1	50	5	0.2	0.1	6	19.50
2	1	80	10	0.4	0.2	7	7.30
3	1	100	15	0.6	0.3	8	4.13
4	1	120	20	0.8	0.4	9	8.05
5	1	150	25	1.0	0.5	10	39.10
6	1.5	50	10	0.6	0.4	10	33.07
7	1.5	80	5	1.0	0.3	9	8.42
8	1.5	100	20	0.4	0.1	7	23.12
9	1.5	120	25	0.2	0.5	6	34.80
10	1.5	150	15	0.8	0.2	8	43.02
11	2	50	15	0.4	0.5	8	28.55
12	2	80	25	0.6	0.4	6	26.51
13	2	100	5	0.8	0.2	9	29.91
14	2	120	10	1.0	0.1	10	10.69
15	2	150	20	0.2	0.3	7	23.42
16	2.5	50	20	0.8	0.1	7	24.93
17	2.5	80	15	0.2	0.3	10	68.34
18	2.5	100	25	1.0	0.5	6	6.84
19	2.5	120	5	0.6	0.2	8	16.34
20	2.5	150	10	0.4	0.4	9	23.73
21	3	50	25	1.0	0.2	9	26.23
22	3	80	20	0.8	0.5	8	32.17
23	3	100	10	0.2	0.4	10	38.95
24	3	120	15	0.4	0.3	7	5.41
25	3	150	5	0.6	0.1	6	15.89
K1	78.53	132.28	90.06	185.01	85.13	103.54	
K2	142.43	142.74	113.74	88.11	122.80	84.18	
K3	119.08	102.95	149.45	95.94	109.72	124.21	
K4	140.18	75.29	111.69	138.08	130.31	96.34	
K5	118.65	145.16	133.48	91.28	141.46	190.15	
R	63.9	69.87	59.39	96.9	56.33	105.97	

When the doping ratio is 15%, the dosage is 0.2 g/L, the initial concentration of NH₃-N is 80 mg/L, the pH is 10, the concentration of H₂O₂ is 0.3 g/L and the illumination time is 2.5h, the removal rate of NH₃-N is up to 68.34%, which is the optimal removal rate. The order of the effect of single factor on NH₃-N removal is as follows: pH> dosage> initial concentration of NH₃-N> illumination time> doping ratio> concentration of H₂O₂.

4. Conclusions

CaF₂(Tm³⁺)/TiO₂ photocatalyst was synthesized using sol-gel method and characterized by SEM and XRD analysis. The crystal form of the catalyst is anatase and the particle size is in the range of 15-25 nm. CaF₂(Tm³⁺)/TiO₂ photocatalyst can effectively degrade NH₃-N in aquaculture wastewater. When

the catalyst doping ratio was 15%, the dosage was 0.2 g/L, the initial concentration of NH₃-N was 80 mg/L, the concentration of hydrogen peroxide was 0.3 g/L, the pH was 10 and the UV light illumination time was 3.0 h, the degradation rate of NH₃-N by CaF₂ (Tm³⁺)/TiO₂ photocatalyst can reach 68.34%.

Acknowledgments

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