

# Photocatalytic Degradation of NH<sub>3</sub>-N in Aquaculture Wastewater by Using CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> under UV Light

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**Abstract.** The TiO<sub>2</sub> doped with CaF<sub>2</sub>(Tm<sup>3+</sup>) photocatalyst is employed to degrade NH<sub>3</sub>-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 CaF<sub>2</sub>(Tm<sup>3+</sup>), dosage, initial concentration of NH<sub>3</sub>-N, pH value, concentration of H<sub>2</sub>O<sub>2</sub> and illumination time on NH<sub>3</sub>-N removal were investigated. The optimal conditions for the degradation of NH<sub>3</sub>-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 NH<sub>3</sub>-N can reach 68.34%. The results show that CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> photocatalyst can effectively remove NH<sub>3</sub>-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, NH<sub>3</sub>-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 NH<sub>3</sub>-N is extremely urgent.

Zhang W[3] used ZnO series as catalysts to treat NH<sub>3</sub>-N wastewater. The results showed that the removal rate of NH<sub>3</sub>-N can reach 66%. Compared with ZnO, TiO<sub>2</sub> 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 TiO<sub>2</sub> makes it widely applied in environmental pollution control[4]. TiO<sub>2</sub> 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 TiO<sub>2</sub> to improve the spectral absorption range of TiO<sub>2</sub>[5]. Many studies have shown that the final product of photocatalytic degradation of NH<sub>3</sub>-N is N<sub>2</sub>[6]. In this study, a TiO<sub>2</sub> doped CaF<sub>2</sub>(Tm<sup>3+</sup>) photocatalyst is employed to degrade NH<sub>3</sub>-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,  $\text{Tm}_2\text{O}_3$ , HF,  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , tetrabutyl titanate(TBOT),  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ .

### 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  $\text{Tm}_2\text{O}_3$  was dissolved in concentrated  $\text{HNO}_3$ . 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  $\text{NO}_3^-$ . 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  $\text{Tm}^{3+}$  to  $\text{TiO}_2$  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.

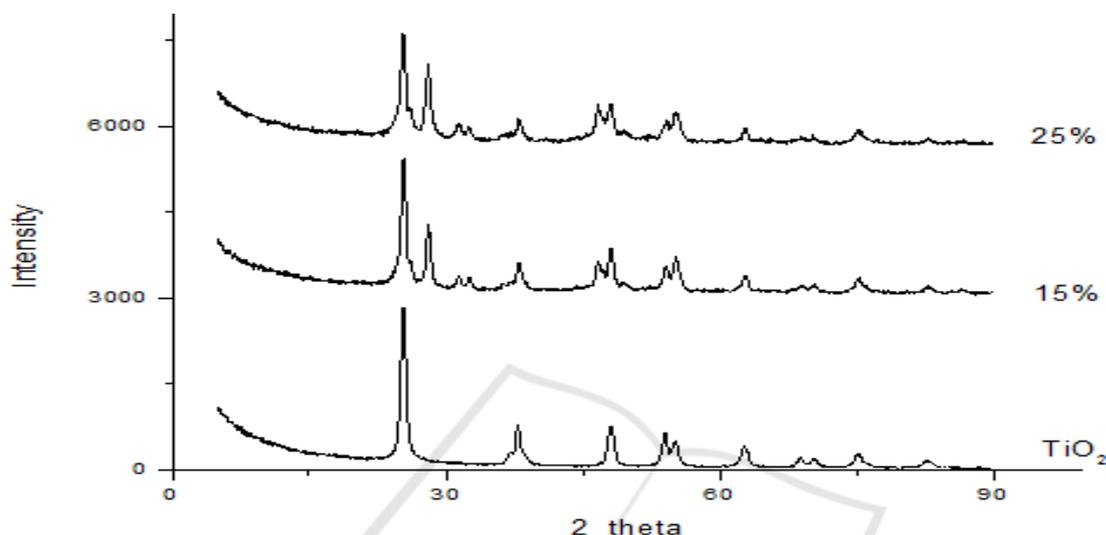
The photocatalytic activity of the  $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$  photocatalyst under UV light (intensity: 18W) was evaluated by measuring degradation of  $\text{NH}_3\text{-N}$  in aquaculture wastewater. According to the experimental requirements, different amounts of  $(\text{NH}_4)_2\text{SO}_4$  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  $\text{H}_2\text{O}_2$  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

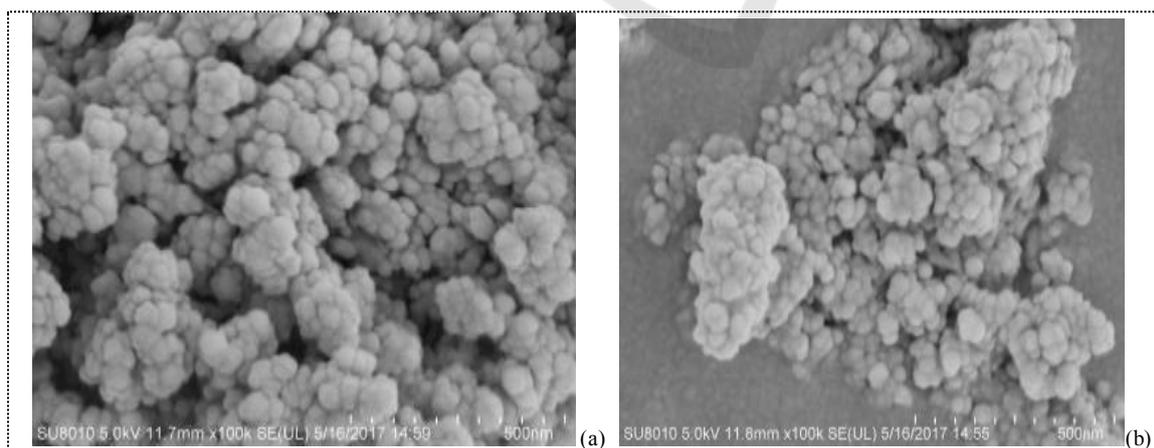
The XRD patterns of materials are shown in Figure 1.  $\text{TiO}_2$  has obvious peaks at  $2\theta$  of  $25.4287^\circ$ ,  $37.8204^\circ$ ,  $47.9708^\circ$  and  $70.3778^\circ$ . The  $\text{CaF}_2(\text{Tm}^{3+})/\text{TiO}_2$  with doping ratio of 15% has obvious peaks when  $2\theta$  is  $25.3284^\circ$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

average particle size of the prepared photocatalyst. The lattice constants a, b and c of TiO<sub>2</sub> 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 TiO<sub>2</sub>, 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 TiO<sub>2</sub> standard (JCPDS No. 89-4921).



**Figure 1.** XRD pattern of CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> photocatalyst with different doping ratios.

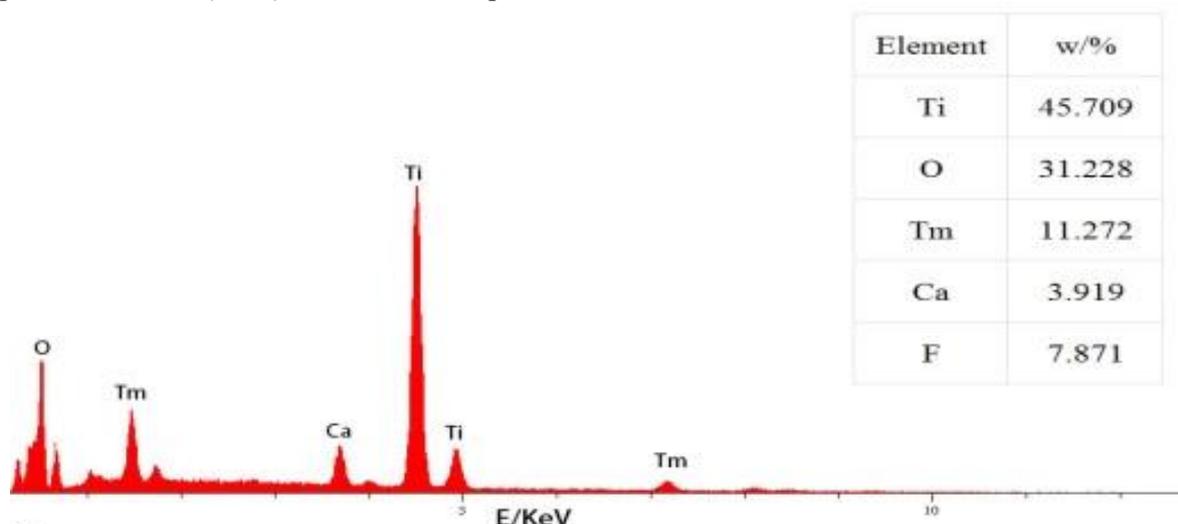
The typical SEM images are shown in Figure 2 (magnification 100 k times). The doping ratios of a, b are 0 and 15% respectively. It can be seen from the figure that the TiO<sub>2</sub> particles display a regular globular structure. Compared with pure TiO<sub>2</sub>, larger particles appear in (b). It can be deduced that the particle size of CaF<sub>2</sub>(Tm<sup>3+</sup>) is larger than that of TiO<sub>2</sub>. Besides, compared with Figure 2a, Figure 2b shows a better crystallinity.



**Figure 2.** SEM images of CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> photocatalysts with different doping ratios.

In order to further determine the presence and relative content of Tm in CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub>, 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  $\text{TiO}_2$ .



**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  $\text{H}_2\text{O}_2$  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%,  $\text{TiO}_2$  is covered with excess upconversion material, which makes the photocatalytic activity of  $\text{TiO}_2$  decrease, so the removal rate decreases gradually.

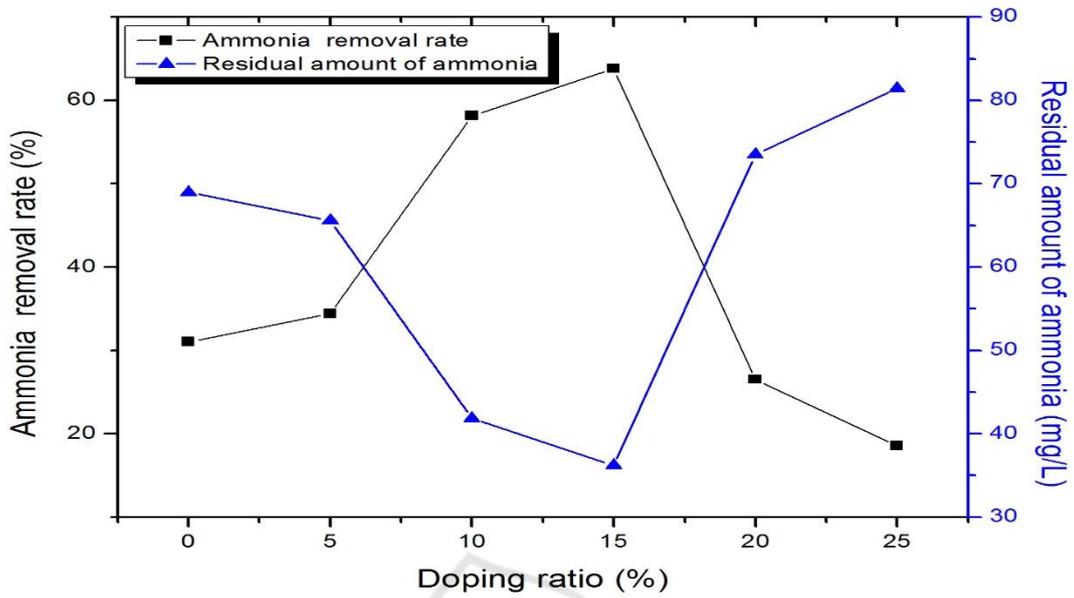
### 3.3. The effect of dosage on photocatalytic reaction

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.

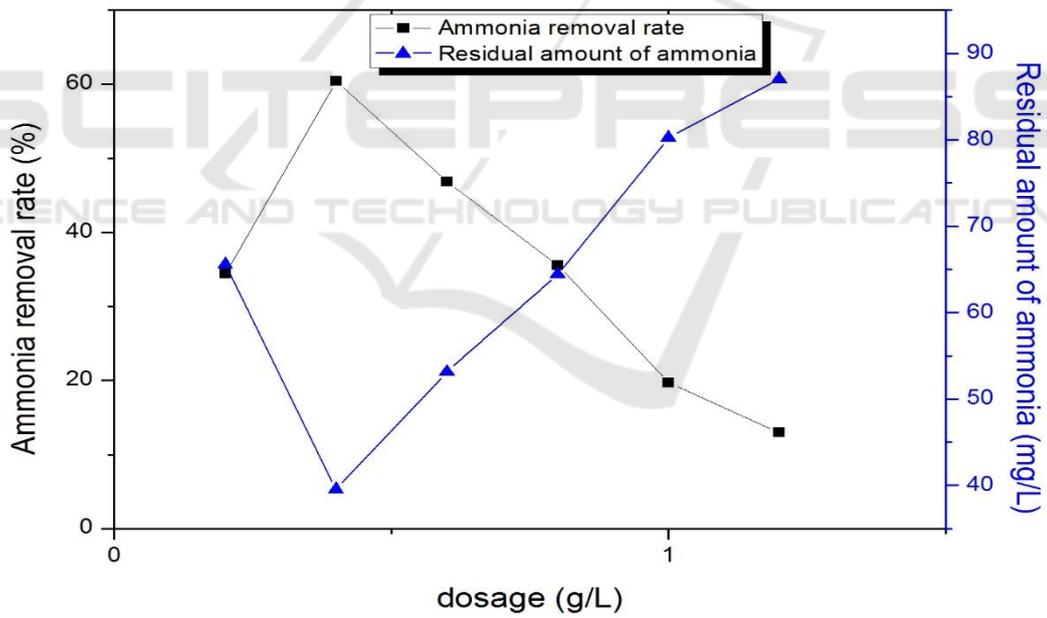
As shown in Figure 4(b), as the dosage increases, the removal increases first and then decreases. The maximum is 60.43% at 0.4 g/L. At the beginning, the removal rate is gradually increased due to the more catalyst involved in the reaction, so that the reaction is carried out more completely. When the 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

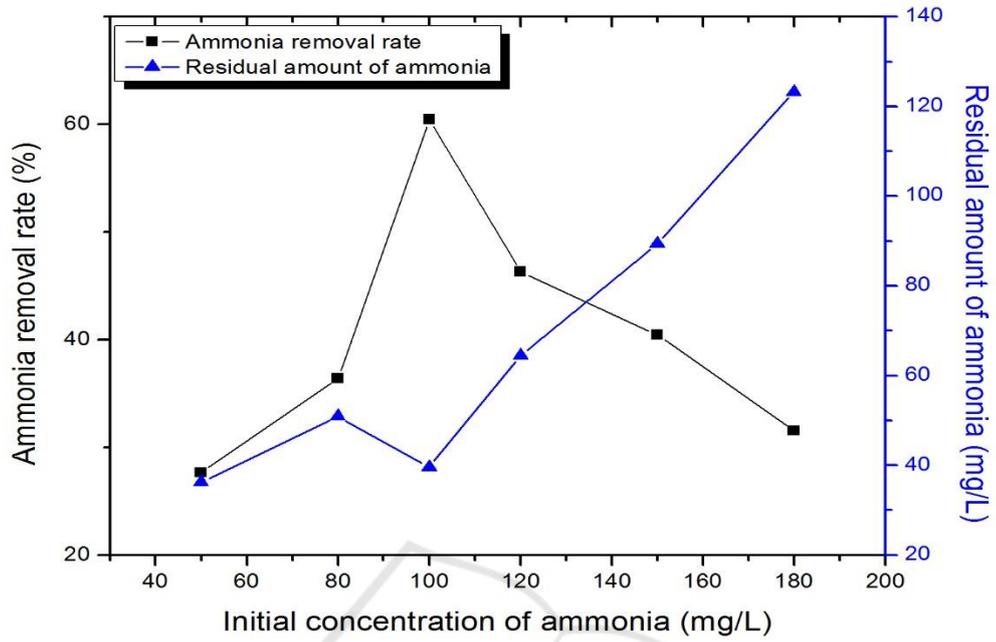
The other conditions were the same as those described in 3.2, just to determine the doping ratio of 15%, the concentration of  $\text{NH}_3\text{-N}$  were 50, 80, 100, 120, 150 and 180 mg/L.



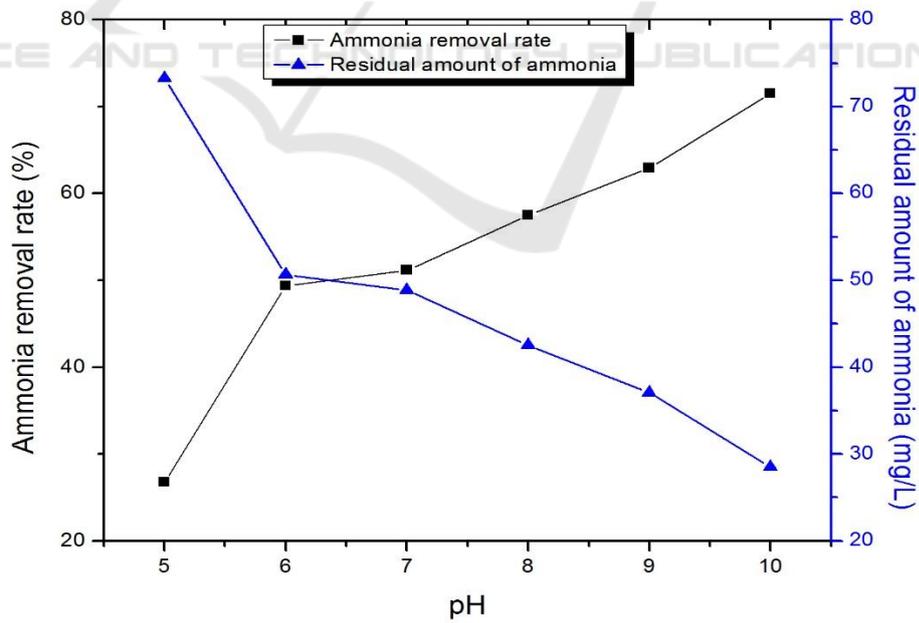
(a)



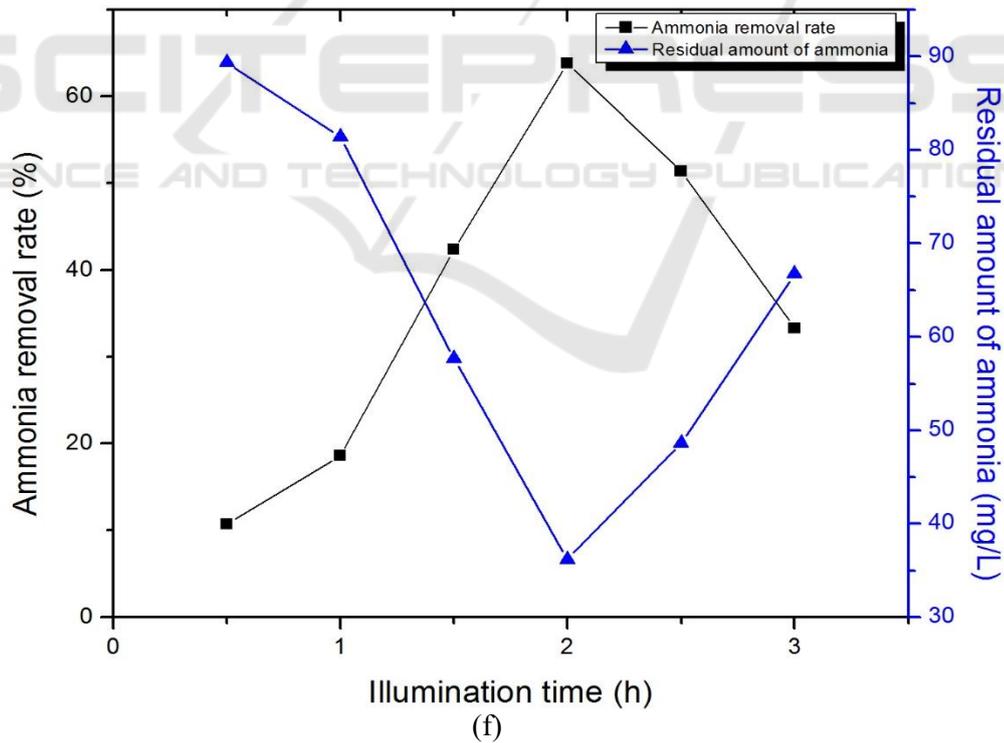
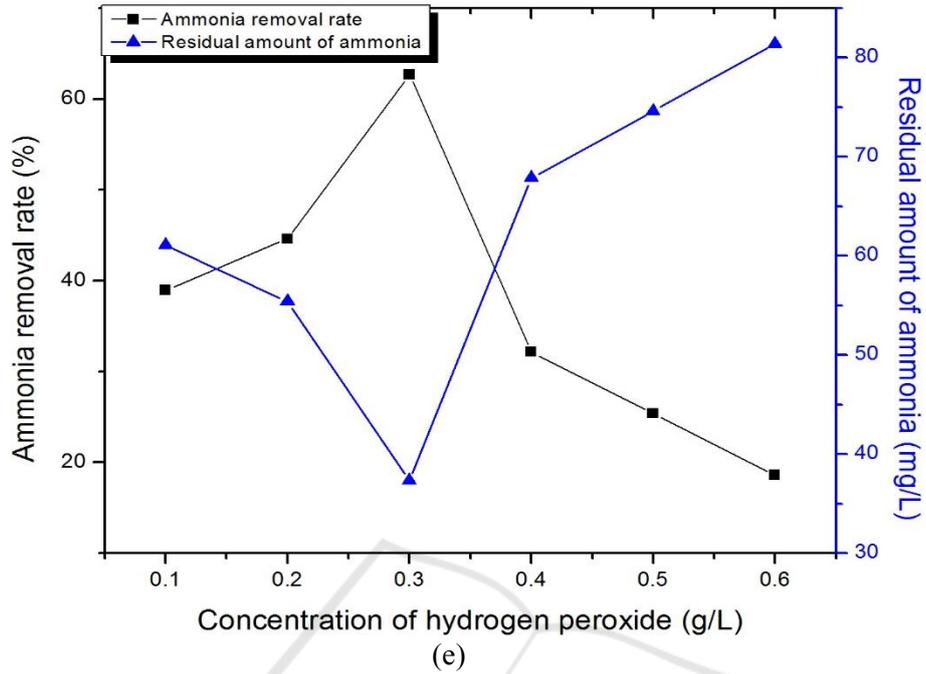
(b)



(c)



(d)



**Figure 4.** Effect of doping ratios of CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub>(a), dosage (b), initial concentration of NH<sub>3</sub>-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  $\text{NH}_4^+$  and  $\text{NH}_3$ . 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  $\text{NH}_3$  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 $\text{H}_2\text{O}_2$ 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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  is 0.3 g/L. Related studies[10] have shown that  $\text{H}_2\text{O}_2$  can promote photocatalytic degradation. As a strong oxidant,  $\text{H}_2\text{O}_2$  will produce a photo-generated electrons capture and result in photo-generated electrons and hole separation[11]. However,  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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 <sub>3</sub> -N/(mg·L <sup>-1</sup> )	Doping ratio/(%)	Dosage/(g·L <sup>-1</sup> )	Concentration of H <sub>2</sub> O <sub>2</sub> / (g·L <sup>-1</sup> )	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 NH<sub>3</sub>-N is 80 mg/L, the pH is 10, the concentration of H<sub>2</sub>O<sub>2</sub> is 0.3 g/L and the illumination time is 2.5h, the removal rate of NH<sub>3</sub>-N is up to 68.34%, which is the optimal removal rate. The order of the effect of single factor on NH<sub>3</sub>-N removal is as follows: pH> dosage> initial concentration of NH<sub>3</sub>-N> illumination time> doping ratio> concentration of H<sub>2</sub>O<sub>2</sub>.

#### 4. Conclusions

CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> 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. CaF<sub>2</sub>(Tm<sup>3+</sup>)/TiO<sub>2</sub> photocatalyst can effectively degrade NH<sub>3</sub>-N in aquaculture wastewater. When

the catalyst doping ratio was 15%, the dosage was 0.2 g/L, the initial concentration of NH<sub>3</sub>-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 NH<sub>3</sub>-N by CaF<sub>2</sub> (Tm<sup>3+</sup>)/TiO<sub>2</sub> photocatalyst can reach 68.34%.

### Acknowledgments

This work has been supported by liaoning province large equipment and equipment sharing service platform capacity building funds, department of science and technology of liaoning (2016LD0105), and science foundation of department of ocean and fisheries of liaoning province (201733), liaoning science and technology public welfare fund (20170002).

### References

- [1] Cui Y, Chen B J and Chen J F 2005 Assessment of self-pollution of mariculture in Huang-Bohai Sea *Chinese Journal of Applied Ecology* 16 (1): 180-185
- [2] Zhang Y, Shi Z, Chen M X, Dong X Y and Zhou J T 2015 Evaluation of simultaneous nitrification and denitrification under controlled conditions by an aerobic denitrifier culture *Bioresource Technology* (175):602-605
- [3] Zhang W, Tang W Y, He S Y, Yang L Z and Xiu R R 2017 Synthesis of ZnO-PMMA composites for photocatalytic removal of ammonia nitrogen at low concentration *Acta Scientiae Circumstantiae* 37( 2) : 664-670
- [4] Gill S H, Young H S, Young U J and Hyun S J 2015 Reduced grapheme oxide/mesoporous TiO<sub>2</sub> nanocomposite based perovskite solar cells *Applied Materials & Interfaces* 7:23521-26
- [5] Li C Q, Sun Z M, Xue Y L, Yao G Y and Zheng S L 2016 A facile synthesis of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> hybrid photocatalysts by sol-gel method and its enhanced photodegradation towards methyl-ene blue under visible light *Advanced Powder Technology* 27( 2) : 330-337
- [6] Chen X H, Liu L F and Yang F L 2007 Removing ammonia nitrogen from water using CdS/TiO<sub>2</sub> photocatalyst *Photographic Science and Photochemistry* 25( 2) : 89-101
- [7] Wei H F, Liu C F and Zhang J X 2013 Improvement of NH<sub>4</sub><sup>+</sup>-N Petermination in Water by Indophenol *Research and Exploration in Laboratory* (7):17-19
- [8] K Nagaveni, G Sivalingam, M.S Hegde and G Madras 2004 Solar photocatalytic degradation of dyes:high activity of combustion synthesized nano TiO<sub>2</sub> *Applied Catalysis B: Environmental* 48(2):83-93
- [9] Zhang W, Tang W Y, He S Y, Yang L Z and Xiu R R 2017 Synthesis of ZnO-PMMA composites for photocatalytic removal of ammonia nitrogen at low concentration *Journal of Environmental Science* 2 (37), 664-670
- [10] Xu Q Q, J Li, M Sun and Yu H 2011 Treatment Effects on Ammonia Nitrogen and Chemical Oxidization Demand using Ultrasonic-TiO<sub>2</sub> Photocatalytic Processes in Landfill Leachate *Environment and Ecology in the three Gorges* 33(2), 27
- [11] Zhang Y, Huang R N, X M Wang, Wang Q and Cong Y Q 2012 Mechanism and Kinetics of Phenol Degradation by TiO<sub>2</sub> Photocatalytic Combined Technologies *Environmental Science* 34(2): 596-603
- [12] Ji Q Y, X C Yu, J Zhang, Liu Y Q, X L Shang and Qi X Y 2017 Photocatalytic degradation of diesel pollutants in seawater by using ZrO<sub>2</sub>(Er<sup>3+</sup>)/TiO<sub>2</sub> under visible light *Journal of Environmental Chemical Engineering* 5(2): 1423-1428