Study on Control of NH$_4^+$-N in Surface Water by Photocatalytic

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Abstract. NH$_4^+$-N has become the main pollution factor affecting the surface water quality in China. Based on the theory of photolysis, the feasibility of photolysis removing NH$_4^+$-N in surface water is studied. The effects of pH, CaO$_2$ content and photolysis time on removal rate of NH$_4^+$-N are studied. The actual study is based on Laboratory studies results. Experimental results show: When the pH<7, photolysis can increase the NH$_4^+$-N content. And when pH>8, the photolysis can greatly reduce the NH$_4^+$-N content in water. CaO$_2$ can greatly remove NH$_4^+$-N. The removal rate of NH$_4^+$-N increased with the increase of photocatalytic time. When irradiated with UV light for 108 hours or the sun is irradiated for about 40 days, NH$_4^+$-N content can be reduced from 4mg/L to 0.5mg/L under the optimum experimental conditions. Adjusting the pH of surface water is the most important condition for controlling NH$_4^+$-N content.

1. Introduction

Ammonia is one of the main elements that cause water eutrophication. With the development of urbanization, large amounts of nitrogen-containing wastewater are discharged, and people develop and use surface water, which seriously undermined the ecological function of the water body [1]. Excess NH$_4^+$-N content in water can cause phytoplankton to multiply, which greatly decrease water transparency and dissolved oxygen content.

It was found that photolysis is an effective and friendly way to remove NH$_4^+$-N in water [2]. Photocatalytic has the advantages of simple operation, no secondary pollution, low energy consumption, stable reaction operation and high removal rate. At home and abroad, study on photocatalytic removal of NH$_4^+$-N has made a series of achievements in scientific research [3]. However, due to the need to use such as TiO$_2$ catalyst, as well as under acidic conditions, this method has been applied to the treatment of industrial wastewater and has not been applied to surface water. In this paper, we studied the surface water with low NH$_4^+$-N content and near neutral condition under UV light source. The feasibility of photocatalytic removal of NH$_4^+$-N in water was studied to provide scientific basis for the removal of NH$_4^+$-N in water by solar energy light.
2. Experimental Part

2.1. Experimental Water
The experimental water body is shown in Table 1.

| Table 1. The parameters of experimental water |
|---|---|---|
| index | No 1 | No 2 |
| T (℃) | 21.1 | 20.2 |
| pH | 7.05 | 7.19 |
| Conductivity (ms/μm) | 4.69 | 6.99 |
| `NH_4^+`-N (mg/L) | 0.08 | 4.05 |
| NO_3^- N (mg/L) | 0.33 | 8.79 |

2.2. Experimental Procedure
1. Preparation of simulated ammonia nitrogen wastewater. The content of NH_4^+ -N was 4 mg/L.
2. Preliminary preparation of the experiment, such as: preparation of solution, experimental equipment and determination of analytical methods.
3. Research on experiment content, including the effect of pH, CaO_2 content, photocatalytic time on Removal of NH_4^+ -N and actual photocatalytic experimental research.

3. Results and Discussion

3.1. Effect of pH Value on Removal of NH_4^+ -N
In the process of photocatalytic removal of NH_4^+ -N in water, pH is an important factor. The pH value of water was adjusted by 2mol/L H_2SO_4 and NaOH before the reaction and photocatalytic time was 8h. Under such conditions, the effect of pH on NH_4^+ -N removal rate was studied, the experimental results are shown in Table 2.

| Table 2. Effects of air on NH_4^+ -N Removal Rate (%) |
|---|---|---|
| pH | Blank control | Confined conditions |
| pH=5 | -7.04 | 0.20 |
| pH=6 | -6.31 | -0.55 |
| pH=7 | 2.15 | -0.13 |
| pH=8 | 5.77 | 3.91 |
| pH=9 | 12.42 | 5.88 |

As shown in table 2, when the pH value was 5~10, the removal rate of NH_4^+ -N increased with the increase of pH value. The pH value of 5~6, NH_4^+ -N removal rate was negative. That is, photolysis promoted the formation of new NH_4^+ -N, and the lower the pH was, the higher the NH_4^+ -N content increased. Under the condition of weak acidity, the photocatalytic activity increases the content of NH_4^+ -N in water, which is due to N_2 in the air generated into NH_4^+ -N and dissolved in water. As Wang Yingli’s [4] research shows, at pH=2, the surface of TiO_2 is protonated and has a positive charge, which inhibits the adsorption of NH_4^+ -OH can’t react with NH_4^+, but it can react with N_2 in the air to form NH_4^+. The experimental study was carried out under the condition of weak acidity without using TiO_2 catalyst. We draw a conclusion that UV, in acidic conditions, can make the water level reduction reaction, resulting in a small number of high reduction free radical: e^-aq and H· [5], which in turn reacts with N_2 dissolved in water to produce ammonia.

When pH is 7~10, NH_4^+ -N removal rate is positive, NH_4^+ -N content decreased, photolysis promoted the removal of NH_4^+ -N in water, and the NH_4^+ -N removal rate increased with the increase of pH value. On the one hand it is because of OH^- concentration increased with the increase of pH. OH^-
increases the content of ·OH by excitation and electron transfer [6]; On the other hand, ·OH generated by photocatalytic reaction and NH3 produced by ammonia hydrolysis will take a dehydrogenation reaction, and reduce NH4+-N content in water. Therefore, with the increase of pH value of water, the content of ·OH and NH3 increased, and the removal rate of NH4+-N increased.

3.2. Effect of CaO2 content on Removal of NH4+-N

UV/H2O2 method [7] is a kind of advanced oxidation method of adding H2O2 in photocatalytic process, which can give full play to the role of photocatalytic. Generally considered: One molecule of H2O2 generates two molecules of ·OH under light irradiation. But H2O2 is easy to decompose in water and has higher cost. CaO2 is a non-toxic, oxygen-releasing and oxidizing environment-friendly inorganic peroxide [8], and will react slowly with water to produce H2O2 and O2. In actual water, CaO2 also has the characteristics of bleaching, deodorization, sterilization and disinfection, as well as effectively removing endocrine disruptors in sludge and improving sludge dissolving efficiency [9]. Therefore, CaO2 was used instead of H2O2 to do the experiment.

Under the condition of pH value of 8 and photolysis time of 8h, the effect of CaO2 on the removal rate of NH4+-N was studied. The effective component of CaO2 particles was 60%, and the content of CaO2 was expressed by N/O ratio (N/O ratio of nitrogen and oxygen). The experimental results are shown in Figure 1.

![Figure 1. Relationship between Removal Rate of NH4+-N and N/O](image)

As can be seen from Figure 1, CaO2 can promote the removal of NH4+-N, and the removal rate of NH4+-N increases with the increase of N/O ratio. When CaO2 content increases to a certain value (N/O=1:4), NH4+-N removal rate gradually tends to be gentle. Studies have shown that CaO2 slowly reacts with water to produce H2O2 in water, and then generates ·OH and O2. Therefore, increasing the content of CaO2 helps to improve the yield of ·OH and promote NH4+-N removal. However, when ·OH concentration is too high, it will trigger side reactions and consume a large amount of ·OH [10-11]. Therefore, when the concentration of CaO2 exceeds a certain value, the trend of increasing the removal rate of NH4+-N gradually tends to be gentle.

3.3. Effect of Photocatalytic Time on Removal of NH4+-N

The experiment was carried out under the condition of pH=8 and N/O=1:4 to study the effect of photocatalytic time on NH4+-N removal rate. The experimental results are shown in Figure 2.
Figure 2. The trend of NH$_4^+$-N removal rate with photolysis time

We can be drawn from Figure 2, with the increase of Photocatalytic time, the removal rate of NH$_4^+$-N gradually increased, and the content of NH$_4^+$-N in water gradually decreased. When the photocatalytic time is about 128h, the average removal rate of NH$_4^+$-N is 96%, and the NH$_4^+$-N content is 0.14mg/L, and remains almost unchanged.

3.4. Actual photocatalytic experimental research

The actual photocatalytic experiment took sunlight as the light source, and a river water in Beijing, Fangshan District is used as test water. The actual photocatalytic experimental study was divided into 6 groups, using 6 glass water tank(30L) as a reaction vessel, No. 1-6. According to the results of laboratory simulation experiment, the pH value of water body was adjusted, and the addition amount of CaO$_2$ was 1:4. No 1, pH=7; No 2, pH=8; No 3, pH=9; No 4, pH=7, N.O=1:4; No 5 pH=8, N.O=1:4; No 6, pH=9,N.O=1:4. The sampling time was 10:00, and the NH$_4^+$-N content was measured every two days. The experimental results of photocatalytic reaction are shown in Figure 3.

Figure 3 The trend of NH$_4^+$-N removal rate with photolysis time

The experiment lasted for 45 days from May 1st to June 14th. As can be seen from Figure 3, with the increase of photocatalytic time, the NH$_4^+$-N content of the 6 groups water decreased gradually. With the increase of the pH value of the water body, the NH$_4^+$-N removal rate gradually increase. CaO$_2$ can greatly remove NH$_4^+$-N. Laboratory simulation results also apply to actual water bodies. Under the conditions of pH value of 8 or 9, N/O of 1:4, the NH$_4^+$-N content decreased from 4mg/L to below 0.5mg/L after 45 days of photolysis, and reached the II class water standard.

4. Conclusion

When pH=7, the photolysis can increase the NH$_4^+$-N content in water. When pH is 8-9, photolysis can obviously reduce NH$_4^+$-N content in water. CaO$_2$ can significantly improve the NH$_4^+$-N removal rate of water, the best N/O is 1:4, that is, the amount of CaO$_2$ added to the water is 17.94mg/L. The content of ammonium nitrogen decreased with the increase of photocatalytic time. When photolysis time was
128h, ammonium nitrogen removal rate was 96%, and ammonium nitrogen content was 0.14mg/l. The sunlight can promote the removal of NH$_4^+$-N in water, and the laboratory conclusion of photolysis is also applicable to the removal of NH$_4^+$-N in the actual water. Under the conditions of pH value of 8 or 9, N/O of 1:4, the NH$_4^+$-N content decreased from 4mg/L to below 0.5mg/L after 45 days of photolysis, and reached the II class water standard.

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