In-depth study of the key factors affecting the degradation of antibiotics by carbon nitride and its modified photocatalytic materials

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Abstract. In this paper, the method of thermal copolymerization is used to synthesize graphite phase carbonitride with urea as precursor, and thermal copolymerization of urea and salicylic acid to form modified carbon nitride. Through a series of experiments to explore the influencing factors of photocatalytic degradation of antibiotics by carbon nitride and its modified photocatalytic materials under different conditions, the suitable experimental and applied catalytic conditions were proposed to provide theoretical support for scientific research and practical application.

1. Introduction
As a bactericidal drug, antibiotics are widely used in people's lives. The production and actual use of antibiotics in China and the world is very large [1]. Abundant antibiotics are difficult to fully absorb and metabolize in humans and animals, and are excreted through excreta [2-3]. Higher concentrations of antibiotics may cause some microorganisms to produce resistance genes that do not degrade into the environment. These resistance genes can spread in the environment, making some pathogenic bacteria resistant to drugs, and thus constitute a greater threat to ecosystems and human health [4-5]. At present, the main methods for removing antibiotics are: photodegradation, hydrolysis, oxidative degradation, sludge adsorption, biodegradation, etc. [6-7]. Among them, photocatalytic degradation technology has the advantages of high catalytic activity, high chemical stability, low cost and low product toxicity, and has become a promising method for pollutant degradation [6, 8-9]. Carbon nitride is a metal-free organic semiconductor. It is chemically and thermally stable. At present, its excellent visible light absorption performance has attracted the attention of many researchers. The study of carbon nitride began with the formula for calculating the solid elastic modulus of sphalerite more than 30 years ago [10]. It has been found that there are five stable carbon nitride structures, namely g-C₃N₄, p-C₃N₄, α-C₃N₄, β-C₃N₄ and c-C₃N₄ [11]. Under natural conditions, g-C₃N₄ is the most stable phase with good photocatalytic properties and is the main research object of carbonitrides.

In this paper, the method of thermal copolymerization was used to synthesize g-C₃N₄ with urea as precursor, and thermal copolymerization of urea and salicylic acid to form modified carbon nitride (SA-C₃N₄). Through a series of experiments to explore the influencing factors of photocatalytic degradation of antibiotics by carbon nitride and its modified photocatalytic materials under different conditions, the suitable experimental and applied catalytic conditions were proposed to provide theoretical support for scientific research and practical application.
2. Experiment

2.1. Equipment and materials
Urea and salicylic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents and materials were of analytical grade and used as received without additional purification or processing. Deionized water (18.25 MΩ·cm) was used throughout the experiment.

The concentrations of tetracycline, ciprofloxacin and enrofloxacin in aqueous solution were detected by UV-2700 (Shimadzu Corporation, Japan). The detection wavelength of tetracycline was 357 nm, and the detection wavelength of ciprofloxacin was 277 nm. The detection of Enrofloxacin wavelength is 270 nm. The concentration of the aqueous sulfamethazine solution was determined by HPLC-UV (HPLC Series 1100 (Agilent, Waldbronn, Germany)), the column packing was C18 (4.6 * 250 mm), the column temperature was 25 °C, and the mobile phase was 0.1% formic acid-water: acetonitrile (80:20, v/v), mobile phase flow rate is 1 mL min⁻¹. The sample injection volume is 20 μL and the detection wavelength is 270 nm.

2.2. Synthesis of g-C₃N₄
10 g of urea was placed in a covered ceramic crucible and then loaded into the center of the muffle furnace. The crucible was first heated to 550 °C with a heating rate of 2.3 °C per minute and held at 550 °C for 4 hours and then naturally cooled. After cooling to ambient temperature, the resulting yellow agglomerate (g-C₃N₄) was ground to a powder.

2.3. Synthesis of SA-C₃N₄
First, 10.0 g of urea and a certain amount (20 mg, 50 mg, 100 mg) of salicylic acid were dispersed in 100 mL of ethanol to form a suspension. The suspension was then stirred at ambient temperature for 2 hours and then sonicated for another hour at room temperature. The suspension was then dried on a hot plate at 90 °C until no significant liquid was found. This calcination process was carried out in the same manner as in Section 2.2 to obtain SA-C₃N₄ (SA-C₃N₄-1, SA-C₃N₄-2, SA-C₃N₄-3).

2.4. Photocatalytic degradation process
The photodegradation activity of the obtained sample was investigated by degrading the antibiotic in an aqueous solution under visible light (>420 nm) under a 300 W Xe lamp. In the photocatalytic degradation experiment, 50 mg of the powder photocatalyst was dispersed in 50 mL of the antibiotic solution. The suspension was stirred in the dark for 1 hour before irradiation to reach an adsorption-desorption equilibrium. Then, the mixture solution was irradiated under visible light. Aliquots were separated from the suspension for a given irradiation time interval.

2.5. Active species trapping experiment
The active substance capture is triethanolamine, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy and isopropanol (IPA), which are introduced as scavengers to detect holes (h⁺), superoxide free radical (·O₂⁻) and hydroxyl radicals (·OH), respectively. The experiment was performed by 1 mM scavenger analysis to degrade antibiotics in aqueous solution under visible light (> 420 nm).

3. Key factors affecting photocatalytic degradation of antibiotics

3.1. Effect of initial concentration of different antibiotics on degradation
Antibiotics use tetracycline as an example. C₀ in the ordinate of Figure 1 is the concentration after the dark reaction, and C is the actual concentration of each sample. It can be clearly seen from the figure that when tetracycline is degraded by photocatalyst SA-C₃N₄-2, the degradation rate and final degradation rate are gradually decreased with the increase of the initial concentration of tetracycline aqueous solution, and the degradation effect was negatively correlated with the initial concentration of tetracycline in aqueous solution. Among them, the aqueous solution of tetracycline with initial
concentration of 5 mg/L showed a rapid decline trend, and the degradation rate was the fastest. The degradation rate was the best at 15 min, with almost 80%, and the final degradation rate was close to 90%, which was about 15% higher than the degradation rate of the tetracycline solution with initial concentration of 40 mg/L. This is because the increase in substrate concentration affects the efficiency of electron transport and indirectly affects the photocatalytic efficiency. Therefore, in practical applications, if the concentration of pollutants is too high when photocatalytic degradation of pollutants, dilution and re-reaction are required.

3.2. Effect of different catalyst additions on the degradation of the same antibiotic
Antibiotics use tetracycline as an example. \( C_0 \) in the ordinate of Figure 2 is the concentration after the dark reaction, and \( C \) is the actual concentration of each sample. From the figure, we can see that when the photocatalyst \( \text{SA-C}_3\text{N}_4-3 \) is used to degrade tetracycline, the ratio of catalyst mass to substrate volume is 1:6 (5 mg photocatalyst), and the degradation of tetracycline aqueous solution is generally effective, and the degradation rate is only 40%, about. The degradation curves of 1:2 (15 mg photocatalyst), 1:1 (30 mg photocatalyst) and 2:1 (60 mg photocatalyst) showed a rapid decline, and the degradation rate of 15 min was better than the ratio. The degradation rate of 1:6, and the final degradation rate are more than 20% higher than the degradation rate of pure CN. Among them, the ratio of 1:1 has the best degradation effect. From the beginning of degradation to 1 h, the degradation rate of the whole process is the fastest, and the final degradation rate is the highest, which was close to 80%. Therefore, it can be concluded that the effect of the catalyst mass to the substrate volume ratio of 1:1 is optimal from the perspective of degradation rate and degradation rate.

3.3. Effect of different initial pH on degradation of the same antibiotic
Antibiotics use tetracycline as an example. \( C_0 \) in the ordinate of Figure 3 is the concentration after the dark reaction, and \( C \) is the actual concentration of each sample. From the figure, we can see that when the photocatalyst \( \text{SA-C}_3\text{N}_4-2 \) is used to degrade tetracycline, the initial pH is 3, the degradation of...
tetracycline aqueous solution is good, and the degradation rate is close to 80%. The degradation curves of initial pH of 6, 8, and 11 showed a rapid decline. The degradation rate of 15 min was better than the degradation rate of initial pH of 3, but the final degradation rate of initial pH of 8 was lower than the initial degradation of initial pH of 3. The rate is slightly worse. The final degradation rates of initial pH 6 and 11 were almost identical and optimal, approaching 80%. Among them, the degradation rate was the fastest at the initial pH of 11 from the start of degradation to 1 h. Therefore, it can be concluded that the initial pH of 6 is optimal from the perspective of degradation rate and degradation rate.

Figure 3. Degradation of tetracycline at different initial pH

3.4. Effect of different pollutants on degradation
For photocatalysts, it is often necessary to degrade many different types of contaminants in actual systems. \( C_0 \) in the ordinate of Figure 4 is the concentration after the dark reaction, and \( C \) is the actual concentration of each sample. From the figure, we can see that in the case of different antibiotics, pure CN and salicylic acid modified SA-C₃N₄-2 degraded enrofloxacin aqueous solution in general, the degradation rate was only 30% and 40% respectively. Pure CN and SA-C₃N₄-2 degraded ciprofloxacin aqueous solution with good concentration, degradation rate reached 45% and 55% respectively; while the effect of pure g-C₃N₄ and SA-C₃N₄-2 degraded sulfamethazine aqueous solution concentration is preferable, the degradation rates are as high as 80% and 95%, respectively. In the case of the same antibiotic, the degradation rate and degradation rate of SA-C₃N₄-2 modified by salicylic acid were better than pure g-C₃N₄, and the final degradation rate was 10% higher than that of pure g-C₃N₄. Therefore, it can be concluded that the effects of pure g-C₃N₄ and SA-C₃N₄-2 on photocatalytic degradation of sulfamethazine in water are superior to other types of antibiotics in terms of degradation rate and degradation rate, and degrade the same species. In the case of antibiotics, the degradation rate and degradation rate of SA-C₃N₄-2 is better than that of pure g-C₃N₄. The faster degradation of sulfamethazine is mainly due to the fact that the -SO₂NH bond is easily destroyed by the catalyst.

Figure 4. Degradation of different pollutants by SA-C₃N₄-2
3.5. Free radical trapping experiment

Antibiotics use tetracycline as an example. C₀ in the ordinate of Figure 5 is the concentration after the dark reaction, and C is the actual concentration of each sample. It can be seen from the figure that in the free-capacity capture test of pure g-C₃N₄, the final degradation rate of the group without the sacrificial agent is about 60%, and the group added with the isopropanol (IPA) does not change with respect to the group without the sacrificial agent. It can be inferred that the number of hydroxyl radicals generated in the photocatalytic reaction is small. By observing the addition of the triethanolamine (TEOA) group and the 4-hydroxy-2,2,6,6-tetramethylpiperidinylxox (TEMPOL) group, it was found that the photocatalytic efficiency was significantly reduced, and the final degradation rate with TEOA added was 50%, and the final degradation rate with TEMPOL was 15%, which was almost one-fourth of that without the sacrificial group. The photocatalytic reaction was strongly inhibited. It can be inferred that the number of superoxide radicals and holes in the reaction process is large, and it is the main free radical that degrades pollutants. In the free radical trapping test of SA-C₃N₄-2, the final degradation rate of the additive-free group was about 80%, and the isopropanol (IPA) group and the triethanolamine (TEOA) group were added to the group without the sacrificial agent. The change is not large, and it can be inferred that the number of hydroxyl radicals and holes generated in the photocatalytic reaction is small. By observing the addition of the 4-hydroxy-2,2,6,6-tetramethylpiperidinylxox (TEMPOL) group, it was found that the photocatalytic efficiency was significantly reduced, and the final degradation rate was about 25%, which is almost a third of the group without the sacrificial agent, the photocatalytic reaction is strongly suppressed. It can be inferred that the amount of superoxide radicals in the reaction process is large and is the main free radical that degrades pollutants. Therefore, it can be concluded that in the process of photocatalytic degradation of tetracycline, the main free radicals of pure g-C₃N₄ degrading pollutants are superoxide radicals and holes, while the main free radicals of SA-C₃N₄-2 degrading pollutants are superoxide radicals.

Figure 5. Degradation of the same antibiotic after adding different sacrificial agents to CN(a) and SA-C₃N₄-2(b)

4. Conclusion and Outlook

Photocatalytic materials have great potential and broad prospects in the treatment of antibiotics in water by visible light catalysis. The utility model has the advantages of high speed, complete decomposition, easy availability of raw materials, mild reaction conditions, simple preparation, wide application conditions, harmless to the environment, low cost, and the like, and has the potential and value of being widely used in treating wastewater containing antibiotics.

In this paper, the preparation of carbonitride photocatalytic materials and their degradation of antibiotics in water are explored. The research progress and different influencing factors of different photocatalysts are explored. From the above discussion, it is easy to see that in practical applications, photocatalytic degradation of pollutants If the concentration of the pollutant is too high, it needs to be diluted and then reacted. The effect of the catalyst mass to substrate volume ratio of 1:1 is optimal from the perspective of degradation rate or degradation rate. The initial pH=6 is optimal from the perspective of degradation rate or degradation rate. The bond is easily destroyed by the catalyst and the degradation
rate is faster. In the process of photocatalytic degradation of antibiotics, the main free radicals of pure g-C₃N₄ degrading pollutants are superoxide radicals and holes, while the main free radicals of SA-C₃N₄-2 degrading pollutants are superoxide radicals. This provides a strong theoretical support for the selection of suitable catalytic conditions for scientific research and practical applications.

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