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Nano-TiO2 Photocatalytic Degradation of Organic Pollutants in Water

Wagenaar Daniel*

The University of Sydney Business School, Australia

**corresponding author*

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Abstract: In order to solve such environmental problems quickly and efficiently, it is imperative to find an economical, environmentally friendly and sustainable solution, and TiO2 photocatalyst has the advantages of cheap, non-toxic and non-polluting. aspects have been extensively studied. The purpose of this paper is to study the development of photocatalytic degradation of organic pollutants in water based on nano-TiO2. The performance of NG/TiO2 composite photocatalyst in degrading organic pollutants acetochlor in water was studied. By studying the adsorption performance, catalyst dosage, H2O2 addition and composite ratio on the photocatalytic degradation of pollutants, the experimental results showed that when the degradation efficiency was the highest when the amount of H2O2 was 2mL. It provides theoretical and experimental basis for the practical application of NG/TiO2 composite photocatalyst.

1. Introduction

It is an effective method to apply nano-TiO2 photocatalytic oxidation technology to sewage treatment. The TiO2 photocatalytic oxidation method uses electrons and holes generated by photo-excited TiO2 and many reactive oxygen species with strong oxidizing ability to reduce impurities [1-2]. The reaction process of photocatalytic degradation of organic matter is very complex, and there are many intermediate products, but the products are different under changing conditions. What is valuable is that many substances can be reduced well, except CO2 and H2O, and the final products include halogen, sulfur, phosphorus and nitrogen, which are the main elements in mineral salts, such as X, SO4- and PO43- respectively [3].

Photocatalysis has received increasing attention from researchers [4]. The experiments of Jouali A were carried out using titanium dioxide (TiO2) immobilized on cellulose fibers in a continuous flow reactor under UV light irradiation. It is emphasized that photocatalytic degradation is unfavorable in acidic media and at too high pH (above pH 12); it reaches the highest efficiency at pH 7.5 (99% and 97% for chestnut and mimosa, respectively). Almost complete degradation of the tannins required an irradiation time of 6 hours. The obtained results suggest that UV light irradiation in a continuous streamer reactor using immobilized titania can be considered as an appropriate method for the treatment of water containing recalcitrant tannin molecules [5]. Imam SS evaluated their photocatalytic efficiency by degrading ciprofloxacin (CIP) aqueous solution (100 mL, 20 ppm), which was placed about 2.5 m away from a 25 W indoor fluorescent light source. During the photocatalytic degradation, Bi/BiOBr-20 achieved a degradation efficiency of 94.8% within 60 minutes, and removed 85.8% of total organic carbon (TOC) after 120 minutes, showing excellent performance [6]. Therefore, it is of practical significance to study the development of nano-TiO2 photocatalytic degradation of organic pollutants in water.

In this paper, NG/TiO2 composite photocatalysts were prepared by effectively controlling the influence factors such as hydrothermal temperature, HF dosage and composite ratio. The NG/TiO2 composite photocatalyst takes full advantage of the high specific surface area and high electronic conductivity of NG, which enables the effective separation of photogenerated electron-hole pairs and increases the adsorption capacity of pollutants, which significantly improves the photocatalytic performance and can effectively Make up for the shortcomings of TiO2.

2. Development of Treatment Methods for Organic Pollutants in Water

2.1. Research Progress of Water Treatment Methods

(1) Traditional physical methods

Distillation technology can remove volatile pollutants without using additional chemicals, but requires more equipment and energy, and the scope of application is restricted by the nature of pollutants [7-8]. Distillation using solar energy can solve the problem of energy consumption. The flocculation method in the physical method is a method in which polyaluminum chloride, polyferric sulfate or high molecular polymer are used as coagulants to coagulate pollutants [9-10]. In this step, the concentration of heavy metals is reduced and small suspended solids form large particles by agglomeration for removal by filtration, sedimentation or flotation [11].

(2) Chemical oxidation method

Chemical oxidation is a method of oxidizing pollutants into harmless H2O, carbon dioxide (CO2) and oxides using oxidants such as hydrogen peroxide (H2O2) and ozone (O3). The cost of reagents and energy of this method is low, it can be carried out under the conditions of normal temperature and pressure, and the sludge produced is also easy to handle. The oxidation method is very effective in the treatment of endocrine disrupting substances such as bisphenol A [12].

(3) Biotechnology

Biotechnology includes bioadsorption technology, biodegradation treatment and enzyme treatment technology. Biosorption technology is a method of replacing high-cost activated carbon adsorbents with biosorbents such as lignocellulose and chitosan [13].

(4) Membrane technology

Membrane technologies include Extractive Membrane Bioreactor (EMBR), Nanofiltration (NF) and Reverse Osmosis (RO). EMBR technology has good potential for removal of phenols. The photocatalytic membrane reactor couples photocatalysis with a membrane separator, which can remove photocatalyst particles from water and act as a barrier. The NF method is used to remove organic contaminants, color and hardness, often before RO units. RO has a good purification effect on industrial wastewater and is often used to separate ions. Membrane technology has low energy consumption and small footprint [14-15].

(5) Advanced oxidation method

Photocatalysis has been found to be an efficient and green technology for water treatment. The catalyst itself is non-toxic and has great potential for fully mineralizing organic wastewater. Moreover, the process does not produce sludge, has short reaction time, saves costs, and works well under normal temperature and pressure [16].

2.2. Nano Preparation Method

Sol-gel method: It uses a compound with higher activity as a precursor to hydrolyze with other raw material reagents to generate monomers, and the active monomers are polymerized to form a stable transparent sol, and after a period of aging, a gel is formed (such as Reaction formulas 1 and 2). Due to the mild reaction conditions of the sol-gel method, it is widely used in the laboratory preparation of nanofilms, nanofibers and composite micro-nanomaterials [17].

$$nTi(OR)_4 + 4nH_2O \rightarrow nTi(OH)_4 + 4nROH \quad (1)$$

$$nHO\text{-}\overset{|}{\underset{|}{Ti}}\text{-}OH + nHO\text{-}\overset{|}{\underset{|}{Ti}}\text{-}OH \rightarrow n\text{-}\overset{|}{\underset{|}{Ti}}O\text{-}\overset{|}{\underset{|}{Ti}}\text{-} + nH_2O \quad (2)$$

The advantages of the sol-gel method are that the reaction conditions are mild, and the hydrolysis reaction occurs at room temperature to prepare sols and gels; various types of nanomaterials can be prepared, including nanopowders, films, fibers, etc.; Nano-films are prepared on substrates of any shape; the prepared reactants are more uniform than other methods, and are very suitable for the preparation of element-doped nano-powders and ultra-fine nano-powders [18].

2.3. TiO2 Photocatalytic Degradation of Pollutants

In recent years, with the development of the national economy, the accompanying environmental pollution problem has become more and more obvious. As a harmless and environmentally friendly semiconductor oxide, TiO2 has good photocatalytic ability to degrade pollutants. The main steps of the electronic transition and catalytic degradation reaction of anatase nano-TiO2 crystals after illumination include:

(1) TiO2 is excited by light to generate hole-electron pairs;

(2) Hole-electron pairs recombine and release energy in the form of heat;

(3) The holes in the valence band cause the oxidation reaction;

(4) The electrons on the conduction band cause the reduction reaction;

(5) Further thermodynamic photocatalytic degradation reaction to mineralize the material;

(6) Ti on the crystal surface captures conduction band electrons to form Ti3+;

(7) The titanol groups on the surface trap the holes in the valence band.

In these reaction steps, the holes in the valence band can react with H2O molecules adsorbed on the crystal surface to generate .OH; the free electrons above the conduction band are easily captured by O2 molecules in the gas to generate O2; these two radicals have Very strong oxidizing properties. When organic pollutants in the environment or organic pollutants in water come into contact with free radicals, the pollutants will be oxidized and decomposed; the TiO2 particles dispersed in the medium will be continuously irradiated by ultraviolet light, and will be continuously irradiated. Free radicals are generated, and environmental pollutants are finally catalyzed and decomposed into small molecular harmless end products such as CO2 and H2O under the continuous oxidation and decomposition of free radicals, so as to achieve the purpose of eliminating pollutants and purifying the environment.

3. Experimental Study on Photocatalytic Degradation of Organic Pollutants in Water by Nano-TiO2

3.1. Experimental Method

(1) Experiment 1

The experiment was divided into 3 groups. The first group first prepared 100 mL of acetochlor solution with a concentration of 50 mg/L, and adjusted pH=9 with diluted sodium hydroxide, and then added 0.2 g of 5wt% NG/TiO2 composite photocatalyst to avoid Light stirring for 60min made it reach the adsorption saturation state. The mixed solution was placed under sunlight, 3 mL of 30% H2O2 was added, and samples were taken every 30 min. After centrifugation, the supernatant was taken, and the absorbance was measured by a UV-Vis spectrophotometer to calculate the photocatalytic efficiency. In the second and third groups, the amount of photocatalyst was adjusted to 0.4g and 0.6g, and the other conditions remained unchanged.

(2) Experiment 2

The experiment was divided into 3 groups. The first group first prepared 100 mL of acetochlor solution with a concentration of 50 mg/L, and adjusted pH=9 with diluted sodium hydroxide, and then added 0.2 g of 5wt% NG/TiO2 composite photocatalyst to avoid Light stirring for 60min made it reach the adsorption saturation state. The mixed solution was placed under sunlight, 1 mL of 30% H2O2 was added, and the absorbance was measured by a UV-Vis spectrophotometer to calculate the photocatalytic efficiency. In the second and third groups, the amount of hydrogen peroxide added was adjusted to 2 mL and 3 mL, and the remaining conditions remained unchanged.

3.2. Test Preparation and Device

(1) Preparation of NG/TiO2 composite photocatalyst

The NG/TiO2 composite photocatalyst was prepared by hydrothermal method. 60 mg of self-made TiO2 powder, NG of different masses (1%, 3%, 5%, 7% and 9% by mass of TiO2, respectively) and 50 mL of deionized water were added to the test tube, and after sonication for 3 hours, the The mixed solution was poured into a 100 mL Teflon-lined reactor and kept at 180 ℃ for 12 hours. Then, the obtained product was centrifuged, washed several times with absolute ethanol and deionized water to remove impurities, and the sample was dried in a vacuum oven at 60 ℃ for 12 h, and the obtained product was the NG/TiO2 composite photocatalyst.

(2) Test device

The small test uses a static cylindrical immersion reactor made of plexiglass, and the outer wall of the device is pasted with aluminum foil. The purpose is to reflect ultraviolet light, improve the utilization rate of ultraviolet light source, and prevent ultraviolet light from leaking out and harming the human body. The cross-sectional diameter of the small test device is 5 cm, the height is 50 cm, and the volume is 1 liter. The schematic diagram of the device is shown in 1.

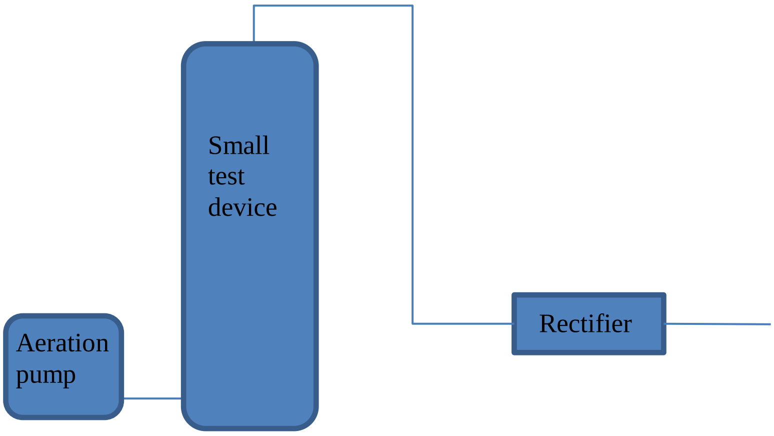

Figure 1. Cylindrical immersed photocatalytic reactor

4. Experimental Analysis on Photocatalytic Degradation of Organic Pollutants in Water by Nano-TiO2

4.1. Degradation Experiments with Different Photocatalyst Dosages

The results of degradation experiments with different photocatalyst dosages are shown in Table 1. When the dosage of photocatalyst is 0.4 g, the degradation efficiency of acetochlor solution is the highest, as shown in Figure 2.

Table 1. Degradation test results of experiment 1

Degradation time/(min)	0.2g	0.4g	0.6g
20	40	55	43
40	44	61	52
60	58	80	77
80	73	89	86
100	81	95	91

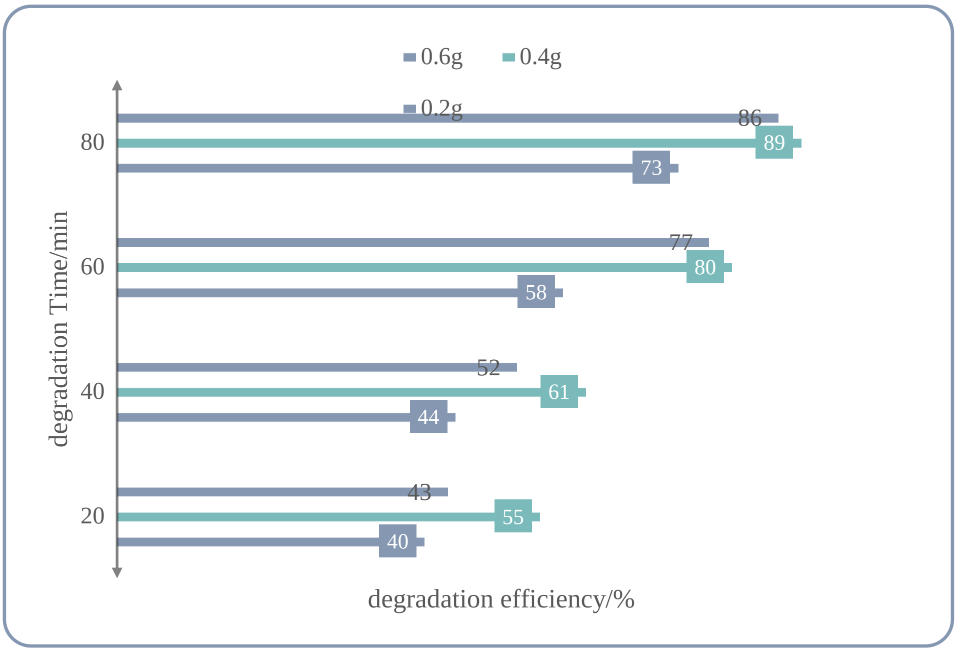

Figure 2. Degradation efficiency of acetochlor with different photocatalyst dosages

Since the photocatalyst is evenly distributed in the acetochlor solution, under the condition of light irradiation, photons will excite electrons to make transitions, forming photo-generated electron-hole pairs, and OH reacts with acetochlor molecules, so as to achieve the the purpose of complete degradation. Within a certain concentration range, with the increase of the amount of photocatalyst, the effective area, active sites and light absorption of the photocatalyst participating in the reaction in the solution increase, and the number of photogenerated hole-electron pairs and OH increases, thereby increasing the number of photogenerated holes and electrons. Effectively improve the degradation efficiency.

4.2. Degradation Experiments with Different Hydrogen Peroxide Additions

OH is a very important free radical with very high oxidation efficiency in the process of degrading organic pollutants. Experiment 2 The results of degradation experiments are shown in Table 2.

Table 2. Degradation test results of experiment 2

Degradation time/(min)	1mL	2mL	3mL
20	21	30	20
40	44	48	40
60	68	72	62
80	81	89	79
100	90	98	88

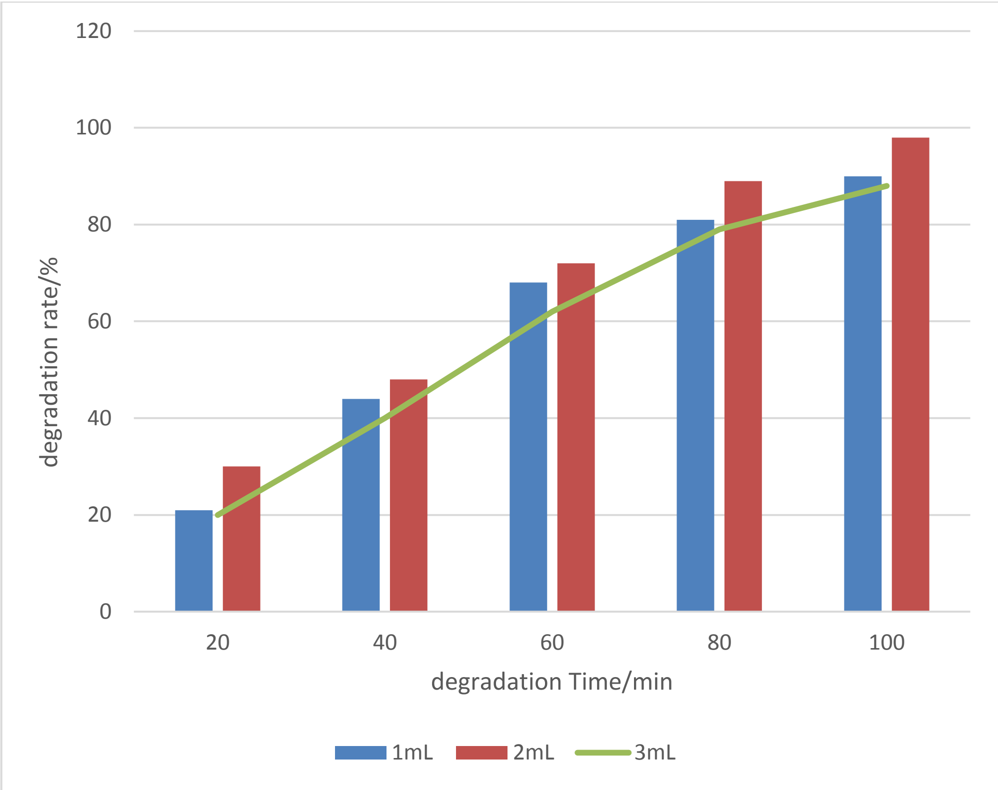

Figure 3. Degradation of acetochlor with different amounts of hydrogen peroxide

It can be seen from Figure 3 that the degradation efficiency of the photocatalytic system is significantly improved with the addition of H2O2, and the degradation efficiency first increases and then decreases with the increase of the addition amount. It remained the same, but the degradation efficiency decreased when the amount of H2O2 was 3 mL.

5. Conclusion

Since photocatalysis has been committed to the development of clean energy from the very beginning to the development of clean energy, photolysis of water for hydrogen production is now closely integrated with environmental protection, and there must be no doubt about its strong vitality and growth potential. The photocatalytic oxidation method studied in this paper is a new type of water treatment technology. The TiO2 film catalyst prepared by the sol-gel method on the surface of the UV lamp has high stability and can be reused, which not only overcomes the shortcomings of suspended phase photocatalysts, and it is easy to improve and scale up for industrial wastewater treatment.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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