Experimental Design of Photocatalytic Teaching for TiO2 Nanomaterials

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Abstract: Because the water quality of industrial wastewater is complex and diverse, it is difficult to treat it, and it is difficult to effectively remove pollutants from industrial wastewater only by traditional water treatment methods. At present, nano-TiO2 photocatalytic technology, which has attracted much attention from researchers in materials and environment, can make up for the shortcomings of traditional water treatment methods and improve the treatment effect of industrial wastewater. TiO2 has high chemical stability, light corrosion resistance and deep valence band energy level. Some endothermic chemical reactions can occur and accelerate on the surface of TiO2 irradiated by light. When it is used in industrial wastewater treatment, it can make up for the shortcomings of traditional treatment methods such as coagulation, precipitation and filtration, and improve the treatment effect of industrial wastewater. Photocatalytic degradation of organic pollutants in the environment is a comprehensive experimental project. This paper introduces the principle and method of the design experiment of photocatalytic degradation of environmental organic pollutants by nano-TiO2, in order to strengthen the cultivation of students' scientific thinking and practical innovation ability.

1. Introduction

With the continuous progress of the industrialization of human society, a large number of industrial wastewater is discharged into the environment. Due to the complex water quality of industrial wastewater, it is difficult to effectively remove pollutants only by traditional treatment methods[1]. At present, the dyes used in industrial production are mostly synthetic organic dyes. Because of the complex composition, high toxicity and high chromaticity of dye wastewater, entering the environment will cause irreversible harm to human life and natural environment[2]. These organic pollutants will exist, accumulate and spread in the natural environment for a long time, and will cause serious harm to human health and ecosystem[3]. Therefore, the treatment of organic pollutants in water has always been an urgent problem in the field of industrial production and environmental treatment. TiO2 is an important chemical raw material closely related to modern life, which has been widely used in industries such as coatings, plastics, paper making, daily chemicals, etc. Moreover, due to its unique semiconductor characteristics, TiO2 has shown a wide application prospect in electronic components, microelectronic sensors, solar converters and so on[4]. TiO2 photocatalytic reaction has the advantages of high reactivity, low energy consumption and no secondary pollution, and has broad application prospects in environmental purification and other fields. TiO2 has high chemical stability, light corrosion resistance and deep valence band energy level. Some endothermic chemical reactions can occur and accelerate on the surface of TiO2 irradiated by light. When it is used in industrial wastewater treatment, it can make up for the shortcomings of traditional treatment methods such as coagulation, precipitation and filtration, and improve the treatment effect of industrial wastewater[5].

Photocatalytic degradation of organic pollutants in the environment is a comprehensive experimental project. The study of TiO2 photocatalysis can not be separated from the test of photocatalyst activity, including the correct measurement of rate constant and activation energy of photocatalytic degradation of organic matter[6]. Therefore, it is very urgent to develop and improve the experimental research technology of TiO2 photocatalysis and standardize the experimental research equipment. TiO2 has excellent photocatalytic activity, and organic matter can be deeply oxidized and degraded by TiO2, and TiO2 is stable to light, non-toxic and cheap[7]. These characteristics make it favored by domestic and foreign academic circles in environmental pollution control, antibacterial and antifouling coatings and self-cleaning building materials[8]. Photocatalysis and nano-TiO2 photocatalyst are one of the important research topics at present. In this paper, the application of nano-TiO2 in the treatment of industrial wastewater is expounded, and it is pointed out that nano-TiO2 photocatalytic technology has become the development trend of industrial wastewater treatment technology, and the photocatalytic teaching experiment of TiO2 nano-materials is designed.

2. Purpose of the Experiment

(1) Understand the existence of organic pollutants in the environment and the treatment methods;

(2) Understand the photocatalytic oxidation technology and its application progress in the environment;

(3) Mastering the method of evaluating the photocatalytic activity of nano-TiO2 by photodegradation experiment;

(4) Familiar with experimental design and data processing methods;

(5) Strengthen the cultivation of students' scientific thinking and practical innovation ability.

3. Experimental Device

At present, the research of TiO2 photocatalysis mainly focuses on two aspects. One is the study of the morphology, structure and composition of photocatalyst, that is, the catalyst with higher activity can be obtained by changing the composition and structure, and it is easier to be practical by improving the catalyst morphology; The second is the kinetic study of photocatalytic process, including the exploration of the mechanism of photocatalytic reaction. Its purpose is to provide information for the further improvement of catalysts and lay the foundation for the engineering design of photocatalytic process through the exploration of the essence of catalytic process. The experimental device designed and assembled by ourselves is shown in Figure 1. The solution to be reacted is placed in a constant temperature jacket for photocatalytic reaction, and a 125W high-pressure mercury lamp is used as the ultraviolet light source for catalytic reaction, and it is made to shine vertically on the reaction solution, and the solution can be taken out for concentration analysis as required at a certain moment of the reaction.

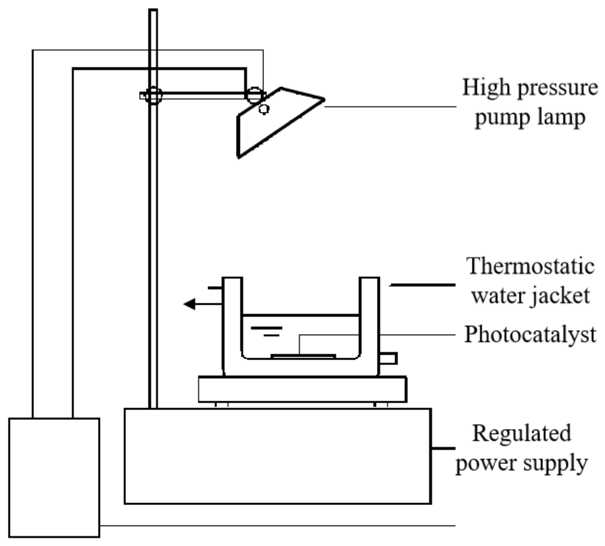

Fig.1 Experimental Device for Photocatalytic Reaction

4. Photocatalytic Principle and Preparation Method of Nanometer TiO2

Photocatalytic oxidation technology uses photocatalyst to generate strongly oxidizing free radicals under the condition of illumination, which can completely degrade almost all organic substances and eventually generate inorganic small molecules such as H2O and CO2[9]. Rutile type and anatase type in nano-TiO2 crystal form have photocatalytic effect, and both belong to tetragonal system, which can be described by octahedron. The difference between their structures lies in the different distribution and assembly of octahedron. When TiO2 is in contact with another phase, the migration mode or path of charged carriers between the semiconductor and the contact phase will change, or be captured at the interface, which will redistribute the charges in the surface layer and form a space charge layer. In order to maintain electrical neutrality, a positive space charge layer will be formed in TiO2, so the electrostatic potential will move and the energy band will bend to the surface. The photochemical or photocatalytic process on the surface of nano-TiO2 begins with light excitation, and the wavelength of the excitation light source is generally in the ultraviolet and visible regions. When the energy radiated by the light source is greater than or equal to the empty energy band between the conduction band and the valence band of the semiconductor photocatalytic material, the photoactive material absorbs the radiation of the light source, and electrons transition from the valence band to the conduction band[10]. As a result, a large number of photogenerated holes are generated in the upper part of valence band, while a large number of photogenerated electrons are generated at the bottom of conduction band. For the reactant molecules adsorbed on the surface of photoactive substances from solution or gas phase, charge is transferred to them through the forbidden band, and photocatalytic reaction is initiated.

Nano-TiO2 photocatalytic technology has a good catalytic degradation effect on organic pollutants. At present, it has been widely used in the treatment of oily wastewater, pesticide wastewater, dye wastewater, surfactant wastewater, papermaking wastewater and other organic wastewater, and can also be used for the recovery and reuse of inorganic compounds in industrial wastewater. Sol-gel method can be used to prepare nano-powder, nano-film, nano-block materials and other nano-materials. The reaction process of preparing nano-TiO2 is as follows: metal compounds that are easy to hydrolyze react with water in a certain solvent, and gradually gel through hydrolysis and polycondensation, and then dry and sinter to obtain the required nano-materials. The hydrolysis process of tetra-n-butyl titanate after condensation is as follows:

$$M(OR)_n + xH_2O \rightarrow M(OR)_{n-x} + xROH \quad (1)$$

Where M is ti; R is an organic group $—C_4H_9$. The reaction can be continued until $M(OH)_n$ is produced.

Measure 18mL of butyl titanate and 40mL of anhydrous ethanol in 100mL beaker to prepare solution A, then measure 40mL of anhydrous ethanol, 4mL of distilled water and 10mL of glacial acetic acid in 500mL beaker to prepare solution B, add A into B drop by drop with stirring, and continue stirring for 30min after dropping, so as to prepare TiO2 gel. Put the gel in an oven at 120℃, dry it for one day, take it out and grind it with a mortar. Then put it in a porcelain crucible and put it in a muffle furnace, and calcine it at 400℃ for 2 hours. Taking out after calcining and grinding into fine powder. The absorbance of organic pollutants in the degradation process is measured by spectrophotometry, that is, samples are taken at regular intervals during the reaction. After centrifugal separation, the supernatant was taken and its absorbance value A was measured at the maximum absorption of organic pollutants by UV-spectrophotometer, which was converted into concentration C according to the standard working curve, and then the degradation rate of organic pollutants after photocatalytic degradation was obtained according to the following formula:

$$X = (C_0 - C)/C_0 \quad (2)$$

Where C_0 is the initial concentration of the solution; C is the concentration (mg/L) of the solution at a certain moment of photocatalytic degradation. The TiO2 photocatalyst was characterized by X-ray diffractometer and ultraviolet-visible spectrophotometer.

5. Experimental Results and Analysis

Fig.2 Is a Typical Ultraviolet Diffuse Reflection Absorption Spectrum of TiO2. Generally, TiO2 Can Absorb Ultraviolet Light with Wavelength Less Than about 400nm.

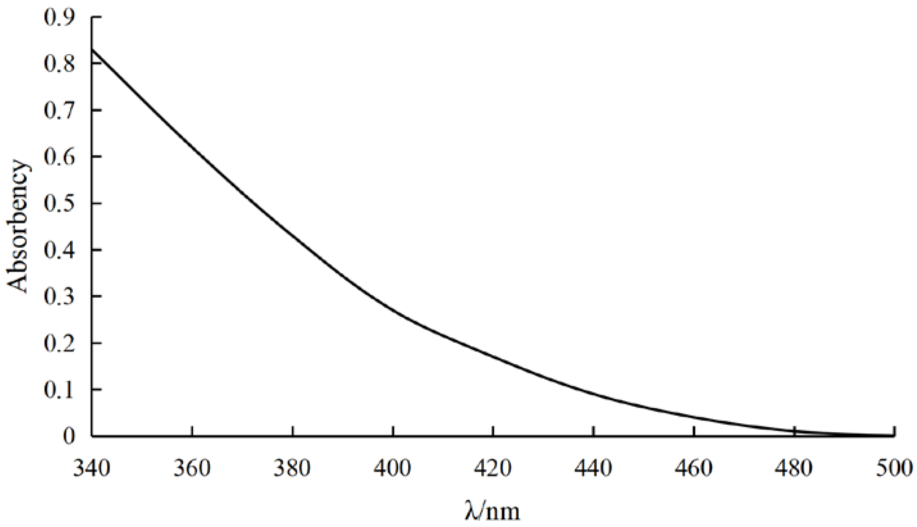

Fig.2 Ultraviolet Diffuse Reflection Absorption Spectrum of TiO2

In the photocatalytic degradation experiment of methyl orange, the concentration of methyl orange at different reaction times was analyzed and the data was processed. The typical results are shown in Figure 3 and Figure 4.

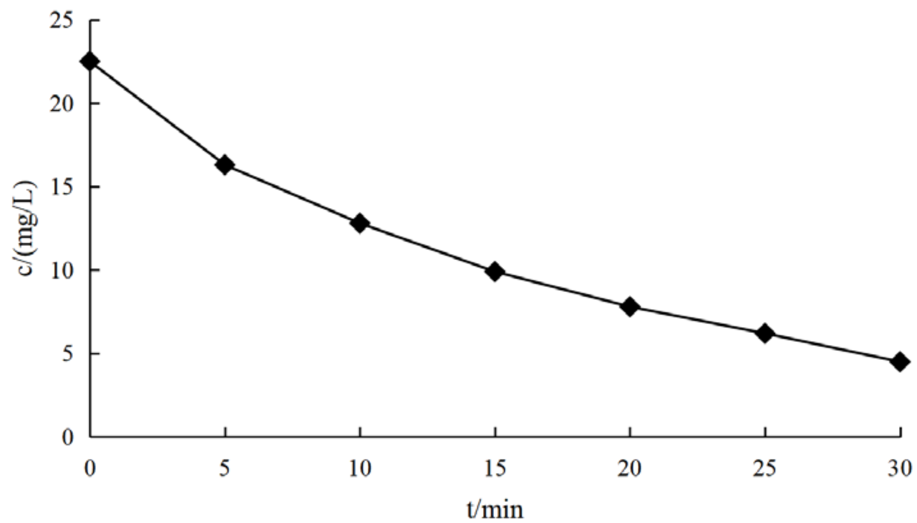

Fig.3 Degradation Curve of Methyl Orange

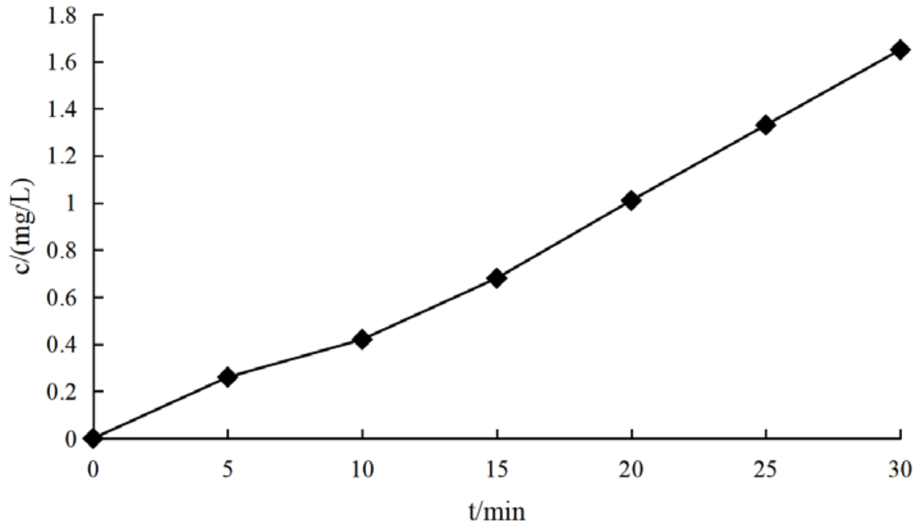

Fig.4 $\ln C_0 / C - t$ Diagram of Methyl Orange Degradation

In Figure 4, the relationship between $\ln C_0 / C$ and t is linear, which shows that the photocatalytic degradation process of methyl orange conforms to the first-order reaction kinetics.

6. Experimental Operation Mode and Content Expansion

To cultivate excellent innovative talents, we need high-quality laboratory resources as the support and guarantee, laboratory management and operation mechanism suitable for talent training mode, and practical measures. Improving the quality of personnel training in an all-round way requires not only the all-out efforts of the laboratory, but also the coordination and cooperation of many administrative departments of the school. It is a complex systematic project and needs constant research and thinking. In this comprehensive experiment, the open experimental operation mode is implemented, that is, the questions are sent to students, and students preview, discuss and experiment. Students first read textbooks, consult relevant books and documents in the library, then design an experimental scheme, discuss it with teachers, and conduct experiments after examination. Open experiment can greatly improve students' initiative and enthusiasm in doing experiments, and they can use their spare time and holidays to do experiments.

According to the specific experimental conditions and class hours, this comprehensive experiment can expand the following experimental contents:

(1) Influence of wastewater pH on degradation rate;

(2) When preparing TiO2, the influence of calcination temperature on its crystal form and photocatalytic activity;

(3) the photocatalytic degradation process of phenol, and the concentration of phenol is determined by high performance liquid chromatography;

(4) The influence of catalyst dosage, methyl orange concentration and pH value on photocatalytic degradation process.

7. Conclusions

In this comprehensive experiment, anatase TiO2 photocatalyst was prepared by sol-gel method. Implementing the open experimental operation mode can greatly improve students' initiative and enthusiasm in doing experiments. In addition, according to the specific experimental conditions and class hours, this comprehensive experiment can also expand the experimental content. The TiO2 photocatalytic reaction device introduced in this paper is simple in structure and convenient to use, and can be used for experimental study of photocatalytic reaction, so as to obtain a series of kinetic experimental data such as photocatalytic degradation rate, photocatalytic reaction rate constant and activation energy. Nano-TiO_2 has its own limitations, such as the low quantum efficiency of TiO_2 in the photocatalytic process, the low utilization rate of visible light energy of TiO_2, and the photocatalytic activity of TiO_2 decreases after repeated use. By doping modification, on the one hand, the spectral range of activated TiO_2 can be broadened, and the light response wavelength can be red-shifted to the visible region, thus reducing the dependence on ultraviolet light sources. At present, there are many researches on nano-TiO_2 photocatalytic technology, but it is rarely used in the practical application of industrial wastewater treatment. In order to make nano-TiO_2 photocatalytic technology really reach the level of practical application, there are still many places to be supplemented and improved. With the continuous development and improvement of the research on nano-TiO_2 photocatalytic technology by scientific researchers, all kinds of unfavorable factors restricting the popularization and application of nano-TiO_2 photocatalytic technology will be improved and solved. Nano-TiO_2 photocatalytic technology will make great contribution to the treatment of industrial wastewater.

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