Photocatalytic Degradation of Industrial Printing and Dyeing Wastewater with Rice Husk-Based Porous Carbon Supported Titanium Dioxide

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Abstract. China has become the world's largest country in the printing and dyeing industry. It is of great practical significance to research and explore effective methods and techniques for treating printing and dyeing wastewater for protecting the water environment and promoting the sustainable development of economy, society and environment. Based on the above background, the purpose of this study is the photocatalytic degradation of industrial printing and dyeing wastewater with rice husk-based porous carbon supported titanium dioxide. In this study, nano-TiO$_2$/AC photocatalyst was prepared by sol-gel method, and the effect and mechanism of removal of methylene blue by TiO$_2$/AC photocatalyst were investigated. The experimental results show that the activated carbon carrier improves the photodegradation efficiency of TiO$_2$. When TiO$_2$ is 0.5 g/L and AC is 0.2 g/L, the photocatalyst has the best photodegradation effect on methylene blue solution; with the initial concentration of methylene blue solution As the temperature rises, the efficiency of catalyst adsorption and photocatalytic degradation decreases. The effect of the three anions on the photocatalytic efficiency is NO$_3^->SO_4^{2-}>Cl^-$. 

Keywords: Nano TiO$_2$, Sol-gel Method, Mechanism Analysis, Catalytic Efficiency

1. Introduction
With the development of society, the kinds and quantity of synthetic toxic and harmful chemicals in industrial wastewater are increasing rapidly, such as benzene, Tsai and anthraquinone compounds in dyestuff, printing and dyeing wastewater, organochlorine and organophosphorus compounds in pesticide wastewater; Nitrobenzene compounds in pharmaceutical wastewater: halohydrocarbon, chlorobenzene, polycyclic aromatic hydrocarbon, aniline, phenol compounds in organic and petrochemical wastewater; copper, cadmium, lead, nickel, thallium, beryllium, mercury, arsenic and their compounds in inorganic chemical wastewater. The common characteristics of these pollutants are high frequency and strong toxicity, with three carcinogenic (carcinogenic, teratogenic, mutagenic) effects, It is difficult to be biodegraded and has a high level of residue in the environment, which can be accumulated in animals and plants. It is called "persistent pollutant". The United Nations Stockholm Convention, the clean water act of the United States and China have listed it on the
blacklist of priority pollutants. Therefore, the research on the treatment of toxic and refractory pollutants in wastewater is a hot issue which has attracted much attention at home and abroad.

The treatment technology of wastewater pollution mainly includes chemical method, physical method and biological method [1-2]. For the industrial wastewater containing toxic and refractory pollutants, traditional chemical and physical methods (sedimentation, flocculation and adsorption) are used to treat it, only to transfer the pollutants from one phase to another phase, which can not completely decompose and harmless the pollutants[3-4]. There are secondary pollution problems, and the treatment cost is high [5]. It is difficult to industrialized operation. The microorganism with special degradation ability for toxic and refractory pollutants has few species and quantity in the treatment system [6-7]. Meanwhile, it is at a disadvantage in interspecific competition, and its removal rate is very low, resulting in a large amount of accumulation in the environment [8-9]. The treatment of this kind of wastewater has been a major technical problem in the field of water pollution control for a long time [10].

In this study, nano-TiO$_2$ supported on active carbon (AC) was used as photocatalyst to study the effect of tungsten doping and anions in solution on photocatalytic degradation of methylene blue and the mechanism of photocatalytic degradation. Graphene oxide was prepared by Hummers method with typical dyestuffs MB and Rhodamine B, and the graphene supported TiO$_2$ catalyst was prepared by two different methods. The morphology and structure of the two catalysts and their photocatalytic activity for methylene blue and Rhodamine B under UV-Vis irradiation were studied. Compared with the photocatalytic activity of nano-TiO$_2$, the two catalysts have higher photocatalytic activity.

2. Method

2.1 Adsorption Method
Activated carbon is famous for its outstanding adsorption performance, which strengthens the adsorption of dye substrate. After the dye substrate is adsorbed, it is photocatalytic degraded by titanium dioxide. The reaction process continuously consumes the active groups and surface charges on the surface of activated carbon, forming an induction effect that is conducive to the migration of photogenerated carriers to the surface, Once the carriers move to the interface, the OH - or O$_2$ adsorbed on the surface of the material can be activated as an active group or photogenerated hole H. Direct oxidation of dye molecules, they have a strong oxidation potential, the benzene ring structure of the dye will be oxidized to open it, and then step by step decomposition, and finally become inorganic small molecules C$_2$O$_2$ and H$_2$O. Photocatalytic degradation becomes the subsequent process of adsorption, because the dye molecules are not easy to form accumulation on the adsorption surface, which overcomes the disadvantage of easy adsorption saturation on the surface of activated carbon, so that it will not cause the extreme increase of viscosity, and it will not cause the problem of difficult cleaning after adsorption saturation of activated carbon, so that the active surface of activated carbon can be regenerated.

According to the principle of photocatalytic regeneration, some researchers have combined the adsorption materials with photocatalyst to treat dye wastewater, organic pollutants, pesticides, etc. This method is mainly to add adsorbent and photocatalyst in the treatment process, and combine the photocatalytic activity of photocatalyst with the adsorption performance of adsorption materials. On the one hand, the adsorption capacity of the adsorbent is enhanced; on the other hand, the adsorption capacity of the adsorbent provides a high concentration for the photocatalytic reaction, improves the photocatalytic reaction rate, and adsorbs the by-products of the reaction to make the pollutants completely purified.

2.2 Special Properties of Nano Semiconductor
Optical properties: the quantum size effect and surface effect of nano semiconductor have great influence on the optical properties of nano semiconductor particles, and lead to some new optical properties of nano semiconductor particles.
(1) Broadband absorption: many nano semiconductor particles (TiO2, ZnO, etc.) have strong absorption of UV light, while the micron level TiO2 hardly absorbs UV light. The absorption of these nano oxides to UV light is mainly due to their semiconductor properties. Under UV irradiation, the electrons are excited, which is caused by the transition of valence band guide band.

(2) Blue shift of absorption edge: compared with bulk materials, the absorption edge of nanoparticles generally has a "blue shift", that is, the absorption band moves to the short wave direction. There are two ways to describe the phenomenon of "blue shift" of the absorption edge of nanoparticles. One is the band gap between the energy level of the molecular orbit occupied by electrons and the molecular orbit not occupied by electrons, which increases due to the decrease of particle size, so that the absorption edge moves towards the short wave direction; the other is the surface effect, because the nanoparticles are small, The large surface tension makes the lattice distortion and the lattice constant smaller, which makes the absorption edge move towards the short wave direction.

(3) Luminescent effect of nanoparticles: when the particle size of nanoparticles is small to a certain value, they can emit light at a certain wavelength.

Photocatalysis: photocatalysis is one of the unique properties of nano semiconductor. Under the irradiation of light, nano semiconductor materials can promote the synthesis of compounds or the degradation of compounds (organic matter, inorganic matter) by converting light energy into chemical energy, which is called photocatalysis. Reducing the particle size of semiconductor catalyst can significantly improve its photocatalytic efficiency. In recent years, the photocatalytic properties of semiconductor nanoparticles such as rn02, ZnO, CDs and PBS have been studied. The results show that the photocatalytic activity of nanoparticles is much higher than that of corresponding bulk materials. The main reasons for the excellent photocatalytic activity of semiconductor nanoparticles are as follows: 1. When the particle size of semiconductor particles is smaller than a certain critical value, the quantum size effect becomes significant, the conduction band and valence band become separate energy levels, the energy gap becomes wider, the energy to generate photogenerated electrons and holes is higher, and it has higher redox ability; 2. The particle size is reduced, and the recombination of photogenerated electrons and holes is reduced, Third, the reduction of the particle size and the increase of the surface area of semiconductor catalyst can promote the photocatalytic reaction.

3. Experiment

3.1 Experimental Instruments and Reagents
Instruments: tu-1810 ultraviolet visible spectrophotometer (HL Jingpu analytical General Instrument Co., Ltd.); arll40 / C electronic analytical balance (ohus international trade company); Philips 70W high pressure mercury lamp; muffle furnace (Shanghai Experimental Furnace Factory); syc-15b super constant temperature water bath (Nanjing sonli electronic equipment factory).

Reagents: methylene blue (chemically pure, Shanghai No.3 reagent plant); Rhodamine B (Shanghai Guoyao group); titanium dioxide (Shanghai Guoyao group); active carbon (model 0970, Ningxia Guanghua Qisi Active Carbon Co., Ltd.); sodium nitrate, sodium sulfate, sodium chloride (analytically pure, Guoyao Group Chemical Reagent Co., Ltd.); graphite powder, kmn04,95% concentrated sulfuric acid, 30% hydrogen peroxide, 5% hydrochloric acid, Tetrabutyl titanate, isopropanol, anhydrous ethanol (analytical pure, Sinopharm Chemical Reagent Co., Ltd.).

3.2 Preparation of TiO2 / AC and w03-TiO2 / AC Catalysts
Firstly, put the activated carbon used in the experiment in the oven 80. C drying for 5h, cooling to room temperature, taking 4G of dry activated carbon, adding 0.35g of n-butyl titanate and 10ml of propanol solvent under stirring conditions, finally slowly dropping 2ml of secondary deionized water, mixing and stirring for 18h, TiO2 / AC catalyst can be prepared. Place the prepared catalyst in the oven 80. C dry for 5h, then transfer to crucible, 450 in muffle furnace. The TiO2 / AC solid
photic catalyst needed for the experiment can be obtained by activating 0.5h at C and cooling to room temperature.

According to the above preparation method, ammonium tungstate was added to TiO2 / AC in the preparation process, and the other preparation process was unchanged. The final solid catalyst was w03-TiO2 / AC composite catalyst required by the experiment. By changing the mass of the added ammonium tungstate, the composite catalyst with different proportion of ammonium tungstate can be obtained.

The whole photocatalytic reaction needs to be carried out in a dark chamber. In the reaction process, add a certain amount of newly prepared methylene blue solution or rhodamine B solution in the constant temperature reactor, and then add a certain amount of adsorbent or composite photocatalyst. Under the condition of magnetic stirring, use 70W high-pressure mercury lamp to irradiate the photocatalysis reaction. In the reaction process, take samples every time, UV Vis was used to measure the absorbance change of methylene blue solution (the maximum characteristic peak was 664nm) or rhodamine B (the maximum characteristic peak was 554nm) at its maximum characteristic peak, and the decolorization rate of dye was used to measure the photocatalytic effect of catalyst. The calculation formula of dye decolorization rate (removal rate) is as follows:

\[
R_d(\%) = \frac{c_0 - c}{c_0} \times 100\% = \frac{A_0 - A}{A_0} \times 100\%
\]  

Among them, \( R_d(\%) \) is the decolorization rate of dye; \( c_0 \) is the initial concentration of dye (mg/L); \( c \) is the concentration of dye at different test time; \( A_0 \) is the absorbance of dye before light; \( A \) is the absorbance of dye at different light time.

4. Discuss

4.1 Effect of AC Dosage on TiO2/AC Photocatalytic Degradation Process

The effect of different amount of AC on the photocatalytic degradation of nano-TiO2 was studied in the solution of 400ml and 50mg / L of MB. Here, the concentration of nano-TiO2 is 0.5g/l. The influence of the amount of AC on the photocatalytic degradation of solid catalyst is shown in Figure 1. It can be seen from Figure 1 that with the increase of AC amount, the decolorization rate of methylene blue also increases. This is because AC can quickly adsorb the MB molecule in water on the surface of catalyst, improve the concentration of MB around TiO2, and increase the probability of contact between TiO2 and MB molecule. The high activity · OH radicals generated by TiO2 photo excitation can rapidly degrade the MB adsorbed on the surface of catalyst, thus improving the degradation ability of catalyst. However, if the amount of AC is too much, the adsorption capacity of the catalyst will increase and the relative concentration of dye molecules around the catalyst will be too large, which will reduce the catalytic efficiency of the catalyst. The optimal AC dosage is 0.29/L.
Figure 1. The effect of AC content on the photocatalytic degradation rate of TiO$_2$/AC

The difference between the parallel determination results is not more than 0.02%. Take the arithmetic average as the measurement result. One of the measured results is shown in Table 1.

Table 1. The relationship between the number of loading nano-TiO$_2$/AC and the amount of loading

| Load times | Load 1 | Load 2 | Load 3 | Load 4 |
|------------|--------|--------|--------|--------|
| 1          | 5.74%  | 8.79%  | 13.08% | 21.24% |

When the loading is 5%-20%, the photocatalyst has the highest photo-assisted oxidation quantum effect. The average value of the loading nanometer TiO$_2$/AC loading amount obtained by loading three times was 11-14% (mass ratio). According to the data obtained from the experiment, select the load 3 times as the best load times.

4.2 Effect of Initial Concentration of Methylene Blue Solution on Photocatalytic Degradation of TiO$_2$/AC

In wastewater treatment, the initial concentration of dye is an important parameter. In this experiment, the appropriate amount of AC was determined to be 0.2g/L, and the amount of nano-TiO$_2$ powder was 0.5g/L. Now it is necessary to determine the effect of different initial concentrations of methylene blue solution on photocatalytic degradation. The initial concentrations of methylene blue solution used in the experiment were 30, 60 and 150 mg/L, respectively. The experimental results are shown in Figure 2.

Figure 2. Effect of initial methyl blue concentration on photocatalytic degradation of TiO$_2$/AC catalyst
It can be seen from Figure 2 that as the initial concentration of methylene blue increases, the decolorization rate of the dye decreases, and the photocatalytic degradation efficiency of the catalyst first rises and then decreases. When the initial concentration of methylene blue is 60mg/L, the photocatalytic reaction is the fastest, while when the concentration of methylene blue is too large, the degradation efficiency of the catalyst is significantly reduced. This is because when the concentration of methylene blue is too high, a large amount of methylene blue molecules are adsorbed on the catalyst surface, which affects the catalytic activity of the catalyst. In addition, the increase in concentration decreases the transmittance of ultraviolet light and the depth of transmission. At the same time, under the condition of high concentration, a large amount of intermediate products will be produced during the degradation process of methylene blue. The competition between adsorption and degradation of methylene blue molecules and intermediate products on the catalyst surface will also lead to a decrease in the photocatalytic rate.

5. Conclusion
In this study, activated carbon (AC), graphene (GE) and conductive carbon fiber (CF) were used as supports, and titanium dioxide (TiO2) was loaded by different methods. The structure and morphology of the catalyst and the photocatalytic degradation of methylene blue and rhodamine B were studied. The study found that activated carbon as a carrier can improve the photodegradation efficiency of TiO2. The initial concentration of methylene blue solution has a great influence on the photocatalytic efficiency. As the initial concentration of the solution increases, the photocatalytic degradation ability of the catalyst increases first and then decreases. In the photocatalytic reaction, the initial concentration of methylene blue solution has an optimal value. Different electrolyte solutions inhibit the photocatalytic degradation of methylene blue solution by the catalyst.

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