Purification of water by bipolar pulsed discharge plasma combined with TiO₂ catalysis

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Abstract. In the process of water treatment by bipolar pulsed discharge plasma, there are not only the chemical effects such as the cold plasma, but also the physical effects such as the optical radiation. The energy of the optical radiation can be used by photocatalyst. Therefore, the effect of the photocatalyst to the degradation of the organic pollutant was investigated using a packed bed reactor by bipolar pulsed discharge in the air-liquid-solid mixture. The nanoparticle TiO₂ photocatalyst was obtained using the sol-gel method and the typical dye solution Indigo Carmine was chosen as the degradation target to test the catalytic effect of the nanoparticle TiO₂ photocatalyst. Experiment results proved that the degradation efficiency of the Indigo Carmine solution was increased by a certain extent with the TiO₂ photocatalyst. It was totally decolorized within 3 minutes by bipolar pulsed discharge in the condition that the peak voltage was 30 kV and the air flow was 1.0 m³ h⁻¹.

1. Introduction
The water treatment by pulsed discharge plasma is a new advanced oxidation technology which includes the features of various advanced oxidation treatment such as electrics, chemistry, optical radiation etc. [1]. Because of several obvious advantages such as mild operating conditions, high processing efficiency, lack of secondary pollution, and non-selectivity for the degradation of organic pollutants, this technology attracts more and more attention and has a broad application prospect [2-6].

Most of previous researches were concentrated on the development of power supply like the DC power and unipolar pulsed power [7-8], or on the development of discharge reactor such as the needle-plate electrode reactor and the coaxial electrode reactor etc. [9]. Besides, the effects of discharge plasma in air and in air-liquid mixture have been extensively studied [10-14]. In our previous studies, the bipolar pulsed discharge in air-liquid-solid mixture system had been proved to be very efficient in decoloration of the dye solution when the “solid” in the system comprises a quantity of glass pellets [15-16]. To make the most of the physical and chemical properties especially the light emission in the reactor to achieve greater removal of organic pollutants and decrease the energy consumption of the power supply, the research of the photocatalyst which could be applied in the discharge plasma is necessary.

In this experiment, the packed-bed dielectric barrier discharge reactor with coaxial electrode configuration was adopted, which takes use of the bipolar pulsed high voltage power supply. A typical dye wastewater Indigo Carmine was chosen to study the purification effect by
bipolar pulsed discharge plasma in the reactor with changed parameters like the peak voltage and air flow, especially to analyze the actual catalysis of the TiO₂ photocatalyst.

2. Experiment system and method

2.1 Experiment system

The experimental setup system is shown in figure 1, which consists of the bipolar pulsed power supply, discharge plasma reactor, the air and water supply system and electrical detection system.

![Figure 1. Experimental setup system.](image1)

![Figure 2. Photo of packing glass pellets.](image2)

1. Bipolar pulsed power supply; 2. Reactor; 3. High voltage electrode; 4. Packing layer; 5. Ground electrode; 6. Air plate; 7. Air inlet; 8. Air outlet; 9. Water inlet; 10. Water outlet; 11. Oscilloscope; 12. High-voltage probe; 13. Current probe; 14. Air flow meter; 15. Air pump

2.2 Experimental method

The pulsed power frequency was 50 Hz and three different applied peak voltages (20 kV, 25 kV, 30 kV) were chosen. Three air flow rates of 0.5 m³ h⁻¹, 0.75 m³ h⁻¹ and 1.0 m³ h⁻¹ were adjusted for the experiment. Our previous experiments had shown that when the diameter of glass pellets was 9 mm, the discharge characteristic in the reactor was better than the status with other diameters [17]. Therefore, the 9 mm’s glass pellets were chosen as the packing layer and two kinds of glass pellets with different surface roughness (labeled 1# and 2# in figure 2) were selected to compare the adhering condition of the nano-TiO₂ film on the surface. The calculated surface roughness data acquired by the provided graphic and analysis tools of MicroXAM-3D was shown in table 1.

| Surface morphological characteristics | Roughness Average, µm | Root Mean Square, µm | Peak-Peak, µm | Density of Summits, µm² |
|---------------------------------------|------------------------|----------------------|---------------|------------------------|
| Data 1#                               | 0.771                  | 0.894                | 8.12          | 0.305                  |
| Data 2#                               | 6.83                   | 8.07                 | 77.0          | 0.202                  |

The sol-gel method was used to prepare the nanoparticle TiO₂ photocatalyst and its catalytic effect was obtained by measuring the absorbance of the target dye solution after being treated in the discharge plasma reactor using the spectrophotometry.
3. Preparation and characterization of photocatalyst

3.1 Catalytic Mechanism of TiO₂ Photocatalyst
When the discharge happened, the cold plasma along with the optical radiation was generated in the reactor. The electron-hole pair was produced when the TiO₂ film absorbed the light emission. On the surface of the glass pellets, a series of reactions were happened as the following equations showed.

\[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + h^+ + e^- \]  
(1)

\[ \text{H}_2\text{O} + h^+ \rightarrow \bullet \text{OH} + \text{H}^+ \]  
(2)

\[ \text{OH}^- + h^+ \rightarrow \bullet \text{OH} \]  
(3)

\[ \text{O}_2 + e^- \rightarrow \bullet \text{O}_2^- \]  
(4)

\[ \text{O}_2 + \text{H}^+ \rightarrow \bullet \text{HO}_2 \]  
(5)

\[ \text{H}_2\text{O} + \bullet \text{O}_2^- \rightarrow \bullet \text{OOH} + \text{OH}^- \]  
(6)

\[ 2 \bullet \text{OOH} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
(7)

\[ \bullet \text{OOH} + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{O}_3 + \text{OH}^- \]  
(8)

\[ \text{H}_2\text{O}_2 + e^- \rightarrow \bullet \text{OH} + \text{OH}^- \]  
(9)

\[ \text{H}_2\text{O}_2 + \bullet \text{O}_2^- \rightarrow \bullet \text{OH} + \text{OH}^- \]  
(10)

Through the reactions above, several very active species were produced like the •OH, •O₂⁻ and •HO₂⁻, which could oxidize the organic pollutants into small molecules because of their strong oxidizability. This was the catalytic mechanism of TiO₂ photocatalyst.

3.2 Pretreatment of Glass Pellets
To make the glass pellets clean enough, they were pretreated as the following steps: clean sufficient number of glass pellets three times with deionized water and place them in ultrasonic cleaning machine for 30 minutes; soak the pellets respectively in 15% hydrochloric acid solution and 20% sodium hydroxide solution for one hour and wash them with deionized water; clean the pellets with ultrasonic cleaning machine for 10 minutes and put them in the drying oven for later use.

3.3 Preparation of TiO₂ Colloidal Sol
Exactly put 85.1 mL tetrabutyl titanate (Ti(OBu)₄) into 175 mL anhydrous ethanol (EtOH), then added 12.8 mL acetyl acetone (AcAc) and 2.25 mL 65% nitric acid (HNO₃) into the solution as the inhibitor to restrain the strong hydrolysis of Ti(OBu)₄ and had the mixture strongly stirred. After one hour, added a mixture of 9 mL water (H₂O) and 87.5 mL anhydrous ethanol with a burette. Stirred the solution strongly for another 2 hours and had the solution static stand for 24 hours at room temperature. After the steps above, a beaker of yellow uniform transparent TiO₂ sol was prepared, in which the concentration of titanium ion is about 0.65 mol L⁻¹. The molar ratio of the substances is Ti(OBu)₄:EtOH:H₂O:HNO₃:AcAc=1:18:2:0.2:0.5. The sol prepared by this method was very stable that could be kept in a closed environment at room temperature for about one year.

3.4 Preparation of TiO₂ Photocatalyst
Put the prepared glass pellets into a funnel of 12 cm in diameter and immersed the funnel into the prepared sol for 3 minutes so that the glass pellets were coated with sol film. Put the pellets in glass dishes and dried them in a drying cabinet at 110 °C for 30 minutes, then took them out to reach the room temperature. Repeat the steps above for three times to ensure that the sol film was thick enough. Roasted the glass pellets in a resistor furnace at 300 for 30 minutes and then at 550 °C for 2 hours. Took the glass pellets out and let them be natural cooling to room temperature. After all the steps, the glass pellets were coated with TiO₂ film on the surface.
3.5 Characterization of TiO₂ Photocatalyst

3.5.1 Surface Morphology of Glass Pellets
The glass pellets coated with TiO₂ film were shown in figure 3. The adhering condition of TiO₂ on the surface of glass pellets labeled 2# was better than that of labeled 1# because of the bigger roughness and the area and thickness of TiO₂ film on the surface of glass pellets coated twice were better than that coated once.

To observe the micromorphology on the surface of the glass pellets when coated with TiO₂ film, the scanning electron microscope was used in the experiment. The SEM images of the glass pellets were shown in figure 4.

It should be specially explained that the SEM images (c) and (f) of the glass pellets’ surface shown in figure 4 were magnified for 100 thousand times. It can be seen from the images that the size of TiO₂ particles, which were aggregated by some smaller particles, was about tens to hundreds of nanometers.
3.5.2 Analysis by XRD

XRD is short for X-ray diffraction, which is used to obtain the information such as composition, internal atomic or molecular structure and morphology by analyzing the X-ray diffraction pattern of target material. The diffraction pattern of TiO₂ film prepared with sol-gel method was shown in figure 5.

![Figure 5. X-ray diffraction pattern of TiO₂ film](image)

As shown in figure 5, there was a strong diffraction peak at the spot where $2\theta = 25.3^o$, which was the characteristic diffraction peak of anatase titanium dioxide’s lattice plane; and there was another strong diffraction peak at the spot where $2\theta = 27.4^o$, which was the characteristic diffraction peak of rutile titanium dioxide’s lattice plane. These results indicated that the TiO₂ film obtained was composed by two kinds of crystal grains: anatase titanium dioxide and rutile titanium dioxide.

The Scherrer equation can be used to calculate the average size of nano-TiO₂ particles through the X-ray diffraction pattern.

$$D = \frac{K \lambda}{B \cos \theta}$$ (11)

In equation (11), $D$ represents the average size of nano-TiO₂ particles (nm); K represents the Scherrer constant, which is 0.89 in usual cases; $\lambda$ represents the wavelength of the X-ray (nm); $B$ represents the full width at half characteristic peak (rad); $\theta$ represents the Prague diffraction angle ($^o$). Take all the parameters into equation (11):

$$D = \frac{0.89 \times 0.15418}{(25.44 - 25.10) \times \frac{\pi}{180} \times \cos 25.3^o} \approx 23.7nm$$

The calculated value showed that the average diameter of the nano-TiO₂ particles was 23.7 nm.

4. Results

4.1 Comparison between Loaded TiO₂ and Powder TiO₂

The comparison of catalytic treatment effect between loaded TiO₂ photocatalyst and powder TiO₂ in the condition that the voltage was 25 kV and the air flow rate was 0.75 m³ h⁻¹ was shown in figure 6. The catalytic degradation effect of indigo solution by adding powder TiO₂ photocatalyst was almost the same with the effect by adding loaded TiO₂ photocatalyst. The method of adding powder TiO₂ was simple and convenient but had the serious disadvantage that the catalyst cannot be recycled which led to a secondary pollution to the environment. In contrast, although the loaded TiO₂ photocatalyst was prepared a little complexly, it overcame the very disadvantage which made it have a broader space for development. Figure 6 proved that the loaded TiO₂ photocatalyst on the surface of the packing glass...
pellets we studied in this experiment was very meaningful.

![Graph](image)

**Figure 6.** Comparison of catalytic treatment between loaded TiO$_2$ photocatalyst and powder TiO$_2$

### 4.2 Influence of Amount of TiO$_2$ Photocatalyst

The amount of TiO$_2$ photocatalyst loading on the surface of glass pellets was an important factor to the catalytic treatment. The glass pellets coated twice had more catalyst on the surface than that coated once. The curves that the time varying absorbance of Indigo solution measured in the condition that air flow rate was 0.5 m$^3$ h$^{-1}$ and voltage was 30 kV or 20 kV were shown in figure 7.

![Graphs](image)

(a) The voltage was 30 kV  
(b) The voltage was 20 kV

**Figure 7.** Influence of amount of TiO$_2$ photocatalyst

As shown in figure 7, in comparison with the condition without catalyst, the degradation rate of dye solution increased obviously when coated with TiO$_2$ photocatalyst and the catalytic effect was a little better when the glass pellets were coated twice than that coated once.

|                  | Without catalyst | Coated once | Coated twice |
|------------------|------------------|-------------|--------------|
| 0.5 m$^3$ h$^{-1}$ 20 kV | 41.26% | 53.90% | 60.38% |
| 0.5 m$^3$ h$^{-1}$ 30 kV | 86.72% | 91.78% | 96.66% |

**Table 2.** Detailed data of degradation ratio
Table 2 showed the degradation ratio of indigo solution after two minutes discharge treatment. When the voltage was 30 kV, the degradation ratio of indigo solution reached 96.66% in the condition that the glass pellets packed in the plasma reactor were coated twice, which suggested that the catalytic effect of the nano-TiO₂ photocatalyst was satisfying.

4.3 Influence of Applied Voltage
The voltage of the power supply was an important factor to the catalytic treatment and its influence was shown in figure 8 with the air flow rate of 1.0 m³ h⁻¹. As the voltage increased, the degradation rate of indigo solution was accelerated and the degradation time was shortened, which suggested that nano-TiO₂ photocatalyst achieved an obvious catalytic effect in the degradation of the dye solution. But the enhanced extent was different in different voltages. The enhanced extent of catalytic effect decreased a little along with the increase of voltage, this was because the discharge was very serious at a high voltage and many indigo molecules had already been resolved in the strong electric field. As a result, the number of indigo molecules that can reach the center of catalyst reduced.

4.4 Influence of Air Flow Rate
The influence of air flow rate to the catalytic treatment effect of nano-TiO₂ photocatalyst in the condition of 20 kV voltage was shown in figure 9. The degradation effect of indigo solution enhanced along with the increase of air flow rate but the enhanced extent was not that much. The promotion of degradation effect of indigo solution by increasing the air flow rate was far less than that by adding TiO₂ photocatalyst. Possible reason was that when the air flow rate increased, the number of bubbles increased and the discharge enhanced in the solution. As a result, the intensity of ultraviolet light generated by the discharge promoted and the catalysis of TiO₂ photocatalyst enhanced by absorbing more ultraviolet light.

5. Discussion
The TiO₂ film on the surface of glass pellets prepared by the sol-gel method was composed by two kinds of crystal grains: anatase titanium dioxide and rutile titanium dioxide, and some anatase TiO₂ will change into rutile TiO₂ at 550 °C. Overall, the adhering condition of TiO₂ on the surface of 2# glass pellets was better than 1# and the amount of TiO₂ film on the surface of glass pellets coated twice was larger than that coated once. From the X-ray diffraction analysis we could calculated that the average diameter of the nano-TiO₂ particles was 23.7 nm, which was the very original size. However, the particles observed by SEM about tens to hundreds of nanometers were aggregated by some particles with smaller size.

Based on the catalytic mechanism of TiO₂ photocatalyst and the surface morphology of the packing
glass pellets by the SEM images, it seemed that the catalytic effect by adding powder TiO₂ should be better than the effect by using loaded TiO₂ photocatalyst. The result in our experiment showed that the two different patterns had almost the same catalytic effect. Possible explain was that the powder TiO₂ dispersed in the discharge plasma reactor lowered the optical transmissivity of the dye solution so that the strongest discharge zone, i.e. the surface of packing glass pellets, absorbed less optical radiation. This negative effect counteracted its original advantage. What should be noticed was that the method of adding powder TiO₂ was simple and convenient but had the serious disadvantage that the catalyst cannot be recycled which led to a secondary pollution to the environment. In contrast, although the loaded TiO₂ photocatalyst was prepared a little complexly, it overcame the very disadvantage which made it have a broader space for development.

6. Conclusion
The purification of dye solution by bipolar pulsed discharge plasma in the air-liquid-solid mixture combined with TiO₂ photocatalyst was investigated using a coaxial electrode configuration. The experiment results showed that the degradation effect was enhanced obviously by the loaded TiO₂ photocatalyst on the surface of packing glass pellets. The catalysis of namo-TiO₂ photocatalyst was influenced by voltage and air flow rate. The enhanced extent of catalytic effect to the indigo solution decreased a little along with the increase of voltage and the degradation effect of indigo solution enhanced along with the increase of air flow. The promotion of degradation effect of indigo solution by adding TiO₂ photocatalyst was far more than that by increasing the air flow rate but a little less than that by increasing the voltage.

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