Study on the Electrochemical Technology and Nanotechnology of Composite Electrode Used as An Alternative to Ultraviolet Light

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Abstract. Advanced oxidation technology has the advantage of being able to efficiently degrade refractory organics, and plays an important role in the treatment of industrial organic wastewater. The article analyses its role in the purification of organic wastewater by the electrochemical method of polymer composite nano-titanium dioxide. The oxygen evolution potential of the nano titanium dioxide electrode is up to 2.8V, showing excellent electrochemical performance. Didache, Si/BDD, Nb/BDD, It/BDD electrodes and surface-modified BDD electrodes can generate strong oxidizing hydroxyl radicals on the surface of the electrodes, which are organic to phenols, dyes, pesticides, and surfactants. The degradability of wastewater is strong. Nano-titanium dioxide electrodes can degrade a variety of organic matter, with a current efficiency of >90%, and can completely mineralize organic matter. Nano-titanium dioxide electrodes have good application prospects in organic wastewater treatment.

Keywords: Polymer composite electrode, nano-titanium dioxide, electrochemistry, oxidation technology, organic wastewater.

1. Introduction
Industrial non-degradable organic wastewater generally has the characteristics of high concentration of organic pollutants, complex components, and poor biodegradability. It is difficult to treat with traditional biochemical methods. Advanced oxidation technology is one of the most promising methods for treating refractory organic wastewater [1]. The core of advanced oxidation technology is the continuous input of external energy (light energy, electrical energy, etc.) and substance (O₃, H₂O₂ etc.), after a series of physical processes and chemical reactions, to produce strong oxidizing hydroxyl radicals ·OH and peroxy radicals (O₂·) Etc., to oxidize organic pollutants in wastewater into CO₂, H₂O and inorganic salts. The oxidation potential of ·OH is as high as 2.8V, which can almost oxidize various organic substances in wastewater, and has a wide range of application prospects.
In the past 30 years, advanced oxidation technology has been widely used in wastewater treatment, including the purification of drinking water, industrial wastewater, groundwater and landfill leachate. The most notable feature is that the oxidant generates free radicals to oxidize and degrade organic substances. The organic free radicals generated by the reaction can participate in the reaction of $\cdot OH$, and can also further generate organic peroxide free radicals. The purpose of oxidative degradation of organic matter. From the perspective of process principles, advanced oxidation technologies mainly include chemical oxidation, photocatalytic oxidation, ozone oxidation, wet oxidation and supercritical water oxidation. With the continuous development of diamond preparation technology and doping technology, BDD film has been successfully deposited on metal, Si, ceramic, graphite and other substrates, becoming a new type of carbon electrode material. Compared with traditional electrode materials, nano-titanium dioxide electrodes have many incomparable excellent characteristics, such as wide electrochemical potential window, low background current, good electrochemical stability, corrosion resistance, and the surface is not easily polluted [2]. Under the electrochemical advanced oxidation technology EAOP can directly mineralize organic matter. Nano-titanium dioxide electrode has opened up a new field for the application of electrochemical methods in wastewater treatment and is a very promising electrode material.

2. The mechanism of extremely oxidizing organic pollutants
The value of the oxygen evolution potential determines the performance of the anode. A necessary condition for a high-quality anode is to have a high oxygen evolution potential. The It/BDD or Di-Chem electrode is the electrode with the highest oxygen evolution potential at present, and it has strong oxidizing ability for organic matter. The mechanism of the nano-titanium dioxide electrode oxidizing organic pollutants is electrochemical combustion, that is, the "active oxygen" (hydroxyl radical $\cdot OH$) physically adsorbed by the organic pollutants on the surface of the electrode generates $CO_2,H_2O$ through electrochemical combustion [3]. Compared with other electrodes, $\cdot OH$ can be generated on the diamond surface and has a high current efficiency CE. This process does not need to add a large number of chemical reagents, does not produce secondary pollution, and does not need to pass oxygen to the cathode, which reduces the number of supporting facilities, so EAOP has more advantages than other electrochemical oxidation processes.

3. Advanced oxidation technology

3.1. Fenton oxidation method
Fenton oxidation method utilizes the reaction of $H_2O_2$ and $Fe^{2+}$ to generate $\cdot OH$, $\cdot OH$ with strong oxidizing properties, which can degrade and even mineralize by reacting with most organic substances. Figure 1 shows the principle of Fenton oxidation. The removal effect of Fenton oxidation on organic matter is affected by factors such as the pH value of the solution, the ratio of the amount of $Fe^{2+}$ and $H_2O_2$ substances, and the reaction time. The advantages of Fenton oxidation method are fast and efficient, can be widely used in all kinds of organic wastewater, improve the biodegradability of wastewater, simple equipment and convenient operation. However, the Fenton oxidation method also has obvious shortcomings [4]. The specific manifestation is that $H_2O_2$ is easy to decompose and inactivate, and is explosive and toxic. It has high requirements for storage and transportation; $Fe^{2+}$ is easy to be oxidized, causing a certain waste of resources; Fenton Oxidation produces sludge, which increases operating costs. Therefore, how to reduce the generation of sludge will become the focus of Fenton oxidation research in the future.
3.2. $O_3$ oxidation method

$O_3$ oxidation is the direct oxidation of organic pollutants with $O_3$, or an indirect oxidation reaction with $gOH$ produced by $O_3$, so as to achieve the degradation of complex macromolecular organics into $CO_2, H_2O$ and small molecular organics. Figure 2 shows the basic principle of the $O_3$ oxidation method.

![Figure 2. Basic principle of $O_3$ oxidation method](image)

The oxidation potential of $O_3$ is 2.07eV, indicating that $O_3$ has strong oxidizing properties and can be effectively used for water disinfection and oxidative decomposition of a series of organic substances. The decolorization effect of $O_3$ for wastewater is obvious, but the degradation effect of COD for organic wastewater is relatively weak. In practical applications, $O_3$ oxidation process is rarely used alone. $O_3 / H_2O_2$, $O_3 /$ catalytic oxidation, $O_3 /$UV, etc. are commonly used combined processes in engineering practice. Therefore, how to improve the efficiency of the combined process and reduce the cost is the focus of future research on $O_3$ oxidation.
3.3. Photocatalytic oxidation method

The photocatalytic oxidation method mainly uses visible light or ultraviolet light in the wavelength range of 290~400nm that can be absorbed by the photocatalyst to stimulate the catalyst electron transition to generate electron holes, and then generate a large amount of strong oxidizing $\cdot OH$ to degrade organic matter in the water. TiO$_2$ is a typical photocatalyst and has a wide range of applications in industry. The effect of pH and TiO$_2$ loading on the degradation of high organic carbon wastewater by photocatalytic oxidation was explored in a small-scale reactor. Research shows that pH has no effect on the removal of COD, and the increase in TiO$_2$ loading can improve the COD degradation efficiency. When the load reaches 1g/L, the COD degradation efficiency can reach 85%. The pilot reactor and industrial reactor have been continuously operated for 30 days. The results show that the COD mass concentration drops from 3000~5000mg/L to 250~300mg/L. The COD removal rate exceeds 90%.

4. The principle of nano TiO$_2$ photocatalytic reaction

Nano TiO$_2$ is an N-type semiconductor material with a wide band gap. Among them, the anatase type is 3.2 eV and the rutile type is 3.0 eV. When it absorbs photons with a wavelength less than or equal to 387.5 nm, the electrons in the valence band will be excited to the conduction band to form a negatively charged highly active electron $e^-$, and at the same time a positively charged hole h$^+$ is generated in the valence band. The oxygen adsorbed on the surface of TiO$_2$ traps electrons to form $\mathrm{O}_2^-$, while the holes oxidize the $\cdot \mathrm{OH}$ and $\cdot \mathrm{H}_2\mathrm{O}$ adsorbed on the surface of TiO$_2$ to form $\cdot \mathrm{OH}$ with strong oxidizing properties. The atomic oxygen and hydroxyl radicals produced by the reaction have strong chemical activity. Oxidative degradation of most organic pollutants. At the same time, the hole itself can also deprive the electrons in the organic substance adsorbed on the surface of the semiconductor, so that the substance that does not absorb light can be directly oxidized and decomposed. These two oxidation methods may work alone or at the same time.

Atomic oxygen, hydroxyl radicals and holes can also react with the organic matter in the bacteria to produce $\mathrm{CO}_2$, $\mathrm{H}_2\mathrm{O}$ and some simple inorganic substances, thereby killing the bacteria and eliminating oil stains. The highly active electrons on the semiconductor surface have a strong reducing ability, and the electron acceptor can directly accept photo-generated electrons and be reduced, so it can be used to remove some specific pollutants in the environment, such as copper ions. In addition, the photon efficiency is related to the time for the excited electrons and holes to reach the surface [5]. As a photocatalyst, the smaller the particle size of nano TiO$_2$, the more electrons and holes reach the reaction surface, and the higher the photocatalytic efficiency. The kinetics of TiO$_2$ catalysing the photo-oxidation and decomposition of organic pollutants generally conforms to the Langmuir-Hinxhe wood kinetic model, that is, the initial rate $r_i$ of the disappearance of pollutants S can be expressed as:

$$
\frac{dc}{dt} = -r_i = \frac{K(S)kSC_i}{1 + K(S)C_i}
$$

Where $C_i$ is the initial concentration of pollutant S, $K(S)$ is the Langmuir adsorption constant of S on the surface of TiO$_2$; $kS$ is the degradation rate constant of pollutant S, in general, $k_i$ is proportional to $I_{a}^{\theta}$, and $I_{a}$ is light absorption Speed, $\Theta$ is a power term, and the value of $I_{a}$ is 1/2 and 1 under strong light and weak light respectively; at the same time, $k_i$ is also proportional to the fraction $\cdot \mathrm{O}_2$ of $\mathrm{O}_2$ adsorbed on the surface of TiO$_2$. The definition of $\cdot \mathrm{O}_2$ is:
Where $K_{O_2}$ is the Langmuir adsorption coefficient of $O_2$. The main features of nano $TiO_2$ antibacterial are: only weak ultraviolet light is required, such as fluorescent lamps, cloudy daylight lamps, etc. to stimulate the reaction; the catalyst itself does not consume, theoretically can be used permanently, without secondary pollution; $\cdot OH$ has 402.8MJ The reaction energy per mol is higher than the energy of various chemical bonds in organic compounds. Therefore, various organic matter can be decomposed into CO2 and H2O, which can kill microorganisms and decompose the organic nutrients that microorganisms rely on for survival and reproduction to achieve antibacterial the purpose of; harmless to the human body.

5. Nano-TiO2 catalytic electrochemical organic wastewater treatment experiment

5.1. The structure of the photocatalytic reactor

The main structure of the photocatalytic reactor is the H2O2/UV/TiO2 system. Under the combined action of chemical oxidation and UV radiation, the oxidation capacity and reaction rate far exceed the effect of using oxidants or UV radiation alone. The key device of the reactor is a photocatalytic oxidation unit. Each unit has a large area of anatase TiO2 solid-supported film. When the wastewater flows in the unit, it contacts the solid-supported film on the inner wall, and photocatalytic oxidation reaction occurs on its surface. At the same time, H2O2 also undergoes oxidation reaction under the action of ultraviolet light to finally remove pollutants [6]. The reactor adopts a modular design, and the number and arrangement of the photocatalytic oxidation unit are determined according to the residence time, the power of the ultraviolet lamp, and the surface area of the TiO2 solid-supported film. At the same time, the specifications of the photocatalytic oxidation unit can also be adjusted according to the amount of wastewater. Figure 3 shows the structure of the titanium dioxide photocatalytic reactor.

![Figure 3. The structure of the titanium dioxide photocatalytic reactor](image)

5.2. Experimental process

5.2.1. The initial concentration of pollutants. Through the experiment of the photocatalytic reactor with different initial concentrations of water, it is found that the concentration of pollutants in the water has a great influence on the photocatalytic degradation rate. The lower the initial concentration of pollutants in the influent, the faster the degradation rate, but the total degradation of pollutants at
low initial concentrations is less than the total degradation of pollutants at high initial concentrations. The change of chemical oxygen demand (COD) and decomposition rate of organic matter after photocatalysis of the inlet water of the regulating tank is shown in Figure 4.

![Figure 4. COD and organic matter decomposition rate changes after photocatalysis](image)

**Figure 4.** COD and organic matter decomposition rate changes after photocatalysis

5.2.2. Oxidant concentration. Adding oxidant is one of the important ways to improve the efficiency of photocatalytic reactor degrading pollutants. To improve photocatalytic efficiency, conduction band electrons and valence band holes must be effectively separated, because oxidant itself is a good electron capture agent. Dosing strengthened oxidant H2O2 can inhibit the recombination of conduction band electrons and valence band holes, and H2O2 itself can directly react with organic matter. The relationship between the dosage of oxidant H2O2 and the removal rate of COD is shown in Figure 5. Through the experiment of changing the dosage of oxidant H2O2, it is found that the degradation efficiency of the photocatalytic reactor increases with the increase of the dosage of oxidant, but when the dosage of H2O2 exceeds 8.0kg/t, the degradation efficiency tends to decrease instead. Therefore, the dosage of H2O2 must be strictly controlled to avoid low photodegradation efficiency due to insufficient dosage, or excessive dosage. High concentration of H2O2 inhibits the reaction and decomposes, causing loss of raw materials.

![Figure 5. The relationship between H2O2 dosage and COD removal rate](image)

**Figure 5.** The relationship between H2O2 dosage and COD removal rate
6. Conclusion
The complexity of industrial wastewater quality determines the difficulty of industrial wastewater treatment. Judging from the existing research results, the advanced oxidation process has achieved satisfactory results in the treatment of industrial refractory organic wastewater, and has a certain generality. However, it is subject to the disadvantages of the high operating cost and relatively harsh reaction conditions of the advanced oxidation process. There is still a certain distance between large-scale industrial applications. TiO2 photocatalytic oxidation technology has outstanding advantages in thoroughly degrading organic pollutants in water and being able to use solar energy. Especially when the concentration of organic pollutants in water is high or it is difficult to treat with other methods, it has more obvious advantages. Unmatched by other traditional methods.

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