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Study on Catalytic Degradation Efficiency and Mechanism of Ofloxacin Using Titanium Composite Electrode

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Abstract

Ofloxacin (OFX) is a third-generation fluoroquinolone antibiotic widely used to treat respiratory diseases and infections. Due to improper discharge treatment, it can be detected in a variety of aquatic environments such as pharmaceutical wastewater and surface water. In addition, ofloxacin is not easily biodegradable, has toxic effects on aquatic organisms and crops, and cannot be fully removed by conventional treatment. Therefore, it is an important research topic to find effective ways to degrade ofloxacin and reduce its harm to human body and environment. Photocatalysis is a technology that uses solar energy to convert light energy into chemical energy, which can effectively remove refractory organic matter in water environment. The single photocatalytic technology has the problems of low conversion of light energy and slow reaction rate, but the photocatalytic technology can reduce the photogenerated carrier recombination by introducing an external electric field, so as to improve the energy utilization rate and reaction rate. In this paper, Ti/SnO_2-Sb (TSSA) electrode material coupled particle electrode was used to realize the treatment of ofloxacin in wastewater containing antibiotics, and the introduction of particle electrode into photoelectric catalysis was explored, and the coupling system was constructed to enhance its catalytic performance.

Keywords

Photoelectrocatalysis; Ofloxacin; Composite Material.

1. Introduction

Antibiotics are widely used, but the lack of a relatively economical and reasonable antibiotic treatment technology has caused great harm to human production and life, so it is very necessary to find a reasonable antibiotic treatment program. In addition, the Henry coefficient value of antibiotics is low, difficult to volatilize, and mostly enriched in water, sediment and soil, which is the way and way of antibiotics in the environment. At the same time, this is also one of the main factors that antibiotics are difficult to remove and increasingly accumulate in the natural environment, so as to affect human health and ecological environment safety. In the past decade, the number of scientific papers on the status of antibiotic pollution and related risks in China's water environment has been increasing, indicating that antibiotics as a new pollutant has gradually attracted people's attention [1].From 2005 to 2016, more than 90 kinds of antibiotics were detected in the water environment in China, with concentrations ranging from 0.1-1000 ng/L[2]. Some studies have detected norfloxacin and other antibiotics in the effluent from wastewater treatment plants in the Pearl River Delta region, and the daily discharge of antibiotics is as high as 1824 g[3]. Tetracycline, sulfonamides, quinolones and macrolides were mainly detected in the surface water environment in China, and their average detected concentrations were 482, 466, 184 and 102 ng/L, respectively [4]. Among them, the average concentrations of ciprofloxacin, Enrofloxacin, norfloxacin and ofloxacin were 42.6, 61.7, 56.3 and 79.2 ng/L, and the maximum concentrations were 899, 536, 655 and 1273 ng/L[5].

Due to the long-term over-dose, over-range and off-label use of antibiotics, the pollution degree of antibiotics in the environment has been maintained at a high level, and even has a rising trend. Therefore, the overuse of antibiotics causes serious pollution problems and poses potential risks to human health and the ecological environment. Ofloxacin is a typical representative of antibiotics. This paper tries to find a suitable treatment method by treating ofloxacin, so as to provide theoretical basis and scientific basis for the treatment of antibiotic pollution in the future.

2. Photocatalytic Technology

PEC is a technology that uses light energy to promote chemical reaction. It is a catalytic technology that combines photochemistry and electrochemistry. It can realize photochemical reaction at normal temperature and pressure, avoid energy waste and environmental pollution in traditional thermochemical reaction, and has the advantages of fast reaction rate, high treatment efficiency and no secondary pollution in environmental treatment . Photocatalysis has been proved to be an effective water treatment technology for the treatment of difficult biodegradable substances and has broad application prospects [6]. The key to photocatalytic methods is to select suitable catalysts. Currently, the commonly used photocatalysts are mainly semiconductor materials, such as titanium dioxide [23], zinc oxide, cadmium sulfide [7], etc. These materials have high photocatalytic activity and stability, but there are some disadvantages, such as large band gap, which can only use ultraviolet light [25]. Due to the high recombination rate of carriers, the photogenerated electron-hole pair cannot effectively participate in the reaction. The number of surface active sites limits the reaction rate. In order to solve these problems, researchers have proposed a variety of optimization strategies, such as doping, loading, compounding, etc. [8]. Titanium dioxide is a commonly used photocatalyst with good chemical stability, thermal stability and dispersibility. But with a wide band gap, it only responds to ultraviolet light. Its energy band structure and surface properties can be adjusted by doping, recombination, loading and other methods to improve its photocatalytic activity and stability, and expand its photoresponse range and application field [9].If you follow the “checklist” your paper will conform to the requirements of the publisher and facilitate a problem-free publication process.

2.1. Principle of Photocatalytic Technology

The whole system of PEC mainly includes optical anode, cathode, power supply, light source and reaction cell. A photoanode is a semiconductor photocatalyst fixed on an electrically conductive substrate (electrode), which must have both an active layer to absorb and utilize light energy and a conductive layer to achieve electron transfer [10]. The cathode is generally a material with good electrical conductivity, and the rapid composite of e^--h^+ can be avoided by selecting appropriate cathode materials as electron acceptors, such as graphite [11], platinum electrodes, etc. The light source mainly provides the energy required for the separation of e^--h^+ in the photocatalyst through a certain intensity of light radiation, and the standard for selecting the light source is based on the band gap and adsorption wavelength of the photocatalyst [12]. The power supply is mainly used to provide a certain voltage or current to promote the transfer of e^- from the optical anode to the cathode. The reaction cell is the place where the photocatalytic REDOX reaction takes place, usually because the light source is external, it is required that the reaction cell should have good light transmission.

The device used to perform photocatalytic processing consists of an electrochemical cell where an external electric potential difference (also known as a voltage) is applied to the electrode, resulting in the formation of reactive substances, namely hydroxyl radicals, near the electrode surface. The process involves the transfer of oxygen from H_2O to organic matter via hydroxyl radicals formed by hydroelectrolysis. Except at high potential, the electrochemical oxidation of certain organics in the water medium can be carried out without loss of electrode activity and is accompanied by the release of oxygen. In addition, it is worth noting that the surface microstructure properties of the electrode material strongly affect the selectivity and efficiency of the process, and the reaction process formula is shown below [13].

2.2. Photoanode Material

As a key part of PEC reaction system, the photoanode has always been the focus of research. The ideal photoanode material should meet the following conditions: (1) the semiconductor has a suitable CB, VB position, suitable Eg; (2) there is a certain conductivity for electron transfer; (3) It has good catalytic activity and mechanical stability to carry out good catalysis and long-term operation. The commonly used photoanode materials in photocatalysis are TiO_2, ZnO, WO_3, CdS[14] and other metal oxides and sulfides.

In photocatalytic systems, anodes usually use composite materials to improve anode chemical stability. Some metals are considered to be chemically stable anode substrate materials, such as niobium, tantalum, titanium, zirconium, etc[15]. It is a very effective method to prepare photoanode by loading active catalyst materials on the metal surface. Ti/SnO_2-Sb anode (TSSA) has proven to be a promising DSA anode with high OEP and low CEP. In addition, it has the advantages of low price and high catalytic activity. Wang et al. used TSSA anode for electrochemical oxidation of ciprofloxacin (CIP). Within 120 minutes, when the current density is 30 $mA \cdot cm^{-2}$, the removal rates of CIP (50 $mg \cdot L^{-1}$), TOC and COD are about 99.5%, 70.0% and 86.0%, respectively [14], among which SnO_2 is a semiconductor material with good performance. It has been extensively studied in the field of photocatalytic wastewater [16].

2.3. Background of Photocatalytic Technology

In the process of photocatalysis, TiO_2 in powder form is usually used, but it is difficult to recover it from the solution after use. In this case, researchers have carried out a lot of studies on TiO_2 film. By loading some substance on the electrode, high treatment effect can be obtained, and it is conducive to recycling[17]. Lu et al. used TiO_2 nanotube array electrodes modified with molecularly imprinted polymers to photocatalyze the degradation of tetracycline, which effectively improved the problem of high E-H^+ recombination rate by applying bias pressure, improved the photoquantum efficiency, and enabled TiO_2 film to be applied to photocatalyze the degradation of antibiotic wastewater [18]. Shih used TiO_2 photoanode to achieve photocatalytic degradation of sulfamethoxazole after 70 minutes under ultraviolet irradiation [19].

2.4. The Application of Photocatalytic Technology

Since the discovery of TiO_2's photocatalytic properties, photocatalysis technology has been considered a promising solution to the challenges of energy crisis and environmental damage. Subsequently, researchers have developed a variety of photocatalysts with excellent photocatalytic properties, such as WO_3[20], $BiVO_4$, Fe_2O_3 and SnO_2[21]. In the case of SnO_2, when the energy of the excited light is greater than the band gap of SnO_2, the electrons in the valence band of SnO_2 will jump to the conduction band, resulting in the separation of electrons and holes[22]. The holes are highly oxidizing, while the electrons are highly reductive and can react with hydroxyl ions (OH^-), water and oxygen on the surface of SnO_2 to form hydroxyl radicals (·OH) with high oxidizing properties. The hydroxyl radicals can then undergo REDOX reactions with organic and inorganic substances on the surface of SnO_2, breaking them down into small molecules, and even directly oxidizing them into H_2O, CO_2, and inorganic salts. Sun et al. synthesized a Z-type SnO_2/Pt/In_2O_3 photocatalyst for the degradation of 2.4-dichlorophenol. 2.4-dichlorophenol removal efficiency under visible light reached 180% within 90 min [23].

Abdullah et al. prepared SB-doped SnO_2 nanoparticles for phenol photodegradation, which could remove more than 95% of phenol within two hours under sunlight irradiation [24]. It can be seen that photocatalysts show broad potential in the field of wastewater treatment. However, the problems of difficult recovery, complex operation and easy recombination of photogenerated electrons and holes limit the large-scale application of photocatalysts.

Photocatalytic technology is a promising method for wastewater treatment. For example, in the photoelectric Fenton system, photocatalysis can cause the reduction reaction of Fe (OH) to form (·OH), thus enhancing the degradation of organic pollutants in wastewater [25]. In photocatalytic wastewater treatment systems, anodes usually use composite materials to achieve high chemical stability. Photocatalysis combines the advantages of photocatalysis and electrocatalysis, and has a broader application prospect as an AOPs processing technology [26]. Based on semiconductor electrodes, excited electrons transition from valence band to conduction band under light, and the rapid recombination of electron-hole pairs during photocatalysis can be effectively inhibited by applying voltage to the anode [27]. There is a synergistic effect between photocatalysis and electrochemistry in the process of photocatalysis. The applied voltage can not only promote the electrochemical degradation of target pollutants, but also facilitate the separation of electron-hole pairs and enhance the electron transfer rate. At the same time, reactive oxygen species are further generated on the electrode surface, which have strong oxidizing properties and have remarkable mineralizing effect on organic pollutants in wastewater, and ultimately transform them into CO_2, H_2O, etc. [28]. In addition, under the action of applied electric field, ionic pollutants can accelerate the migration to the electrode, which promotes the degradation of pollutants.

3. Fluoroquinolone Antibiotic Ofloxacin in Water Environment

3.1. Source and Characteristics

Ofloxacin can be released into environmental water bodies through a variety of ways, such as biological metabolic waste, sewage treatment plant effluent, agricultural residues, industrial pharmaceutical wastewater and so on. Among them, human or other biological waste and wastewater discharge are the two main ways to enter the environment [29]. On the one hand, in the field of human allotherapy and veterinary medicine, antibiotics are widely used, and ofloxacin ingested in humans and animals is not fully absorbed, most of it is excreted through urine and feces, and a large part of ofloxacin in these faeces exists in its original form and active form, and a part of the faeces will enter the sewer and eventually flow into domestic sewage treatment plants. The removal efficiency of ofloxacin is very low because the removal amount is affected by the sewage treatment rate of each city and the removal efficiency of the target chemical in the sewage treatment plant. Another part of the excrement will be discharged directly into streams or discarded in solid form on farmland, and ofloxacin will enter groundwater through surface water infiltration and migration and soil leaching. On the other hand, in the discharge process of medical, pharmaceutical and agricultural wastewater, part of the wastewater is discharged after treatment by the sewage treatment plant. Because there is no discharge index for emerging pollutants such as ofloxacin in the current sewage discharge standard, the wastewater containing ofloxacin will enter the water body environment with the tail water of the sewage treatment plant. On the other hand, due to lack of supervision or human factors, some industrial and agricultural production wastewater may directly enter the surface water environment [30].

3.2. Structure and Toxicity Analysis of Ofloxacin and its Intermediate Products in Antibiotics

Ofloxacin has covalent bonds in its molecular structure, which is difficult to degrade, and its appearance is slightly yellow crystal. Density 1.5 ± 0.1 g· cm^{-3}, melting point 270~275 ℃. Soluble in glacial acetic acid, insoluble in water, insoluble in ethyl acetate [31]. As a typical representative of quinolones, ofloxacin contains characteristic quinolone rings within its molecules. At the same time, because of the F atom in the C-6 position, ofloxacin is also classified as a fluoroquinolone antibiotic. The combined action of piperazine and fluorine atoms at the C-7 position can enhance the effectiveness of ofloxacin against bacteria [32]. The following figure shows the 3D molecular structure of Ofloxacin.

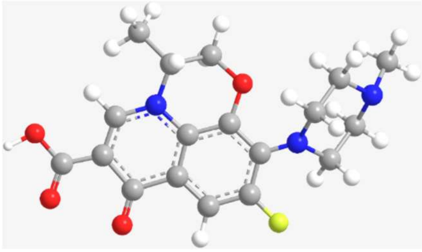

Fig. 1 3D molecular structure diagram of ofloxacin

Ofloxacin has a variety of functional groups, including -F, -COOH, C=O, C=C, benzene ring, etc., which can undergo a variety of chemical reactions. For example, -F is easy to undergo substitution reactions, benzene ring, C=O and C=C can all undergo addition reactions, and H on the benzene ring can be replaced. It is worth noting that the characteristic quinolone ring has a stable structure and low reactivity, which makes ofloxacin difficult to be hydrolyzed and has excellent stability. Therefore, it is extremely difficult for ofloxacin to be degraded naturally when it enters the water environment [33]. At the same time, the efficiency of the traditional water pollution treatment process is also very low, and the wastewater containing ofloxacin will still be discharged into the surface water environment with the tail water after entering the sewage treatment plant.

4. Material Preparation and Analysis

4.1. TSSA Electrode Preparation

The main steps of the titanium mesh pretreatment were as follows: The titanium mesh was washed in 5%NaOH solution at 90°C for 1 h;Then, the titanium mesh is immersed in 10% oxalic acid solution and soaked at 90°C for 1.5 h (the solution gradually turns black);The etched titanium mesh was washed with deionized water (DI), and ultrasonic cleaning was carried out in deionized water for 30 min.The cleaned titanium mesh is dried in a 100°C oven and stored in anhydrous ethanol.The preparation method of anodic photocatalytic coating solution is as follows:4.7594 g $SnCl_2 \cdot H_2O$ and 9.3076 g citric acid were added to a conical bottle containing 40 mL glycol and 1 mL concentrated hydrochloric acid. The mixture requires magnetic stirring and condensation reflux at 60°C for 3 hours.After 3 h, 0.2406 g SbCl3 was added to the above mixture and continued stirring at 60°C for 2 h.The obtained solution is sealed and stored overnight, and the coating solution is prepared.The brushing and sintering steps are as follows:Apply the coating solution to the treated titanium net with a brush, then put the titanium net coated with the coating solution into the oven, dry at 100°C for half an hour, remove the titanium net and scrub again, repeat 5 times.

4.2. Electrode Analysis Method

The catalyst was characterized by X-ray diffraction analysis, scanning electron microscopy, X-ray electron spectroscopy, UV-visible diffuse reflection spectroscopy and electrochemical testing.The photoelectric catalytic system is constructed with light source, electrolytic cell and DC voltage regulated power supply. The anode uses TSSA electrode and the cathode is graphite electrode for degradation. At the same time, magnetic stirring is carried out to keep the solution uniform. The influence of different initial concentration, applied bias, pH, electrolyte concentration and other factors on photocatalytic degradation of ofloxacin was studied by using control variable method, and the cyclic stability of anode was tested. Finally, the main active free radicals of photocatalytic degradation of ofloxacin were studied by adding free radical quencher.

4.3. Study on Degradation and Mechanism of Ofloxacin

With a new photoelectric catalytic oxidation reactor as the core, a photoelectric catalytic oxidation system was constructed, and ofloxacin degradation experiment was conducted to explore the degradation ability of the prepared TSSA electrode, and the electrode after reaction was characterized again to explore the reuse performance of the anode material, and explore the application of different experimental conditions[20]. For example, pH, initial concentration of wastewater, current density, light intensity, electrolyte type, plate spacing and other influences on the efficiency of ofloxacin degradation, the degradation rate of ofloxacin was used as an indicator to determine the optimal reaction conditions and explore the best treatment process for the degradation of ofloxacin.

4.4. Mechanism Analysis

Photocatalytic removal of pollutants in water mainly depends on the strong oxidizing active substances produced in the catalytic system. When the catalyst is photoelectric excited, its band gap e- transitions from its own VB end to CB end, the formed photogenerated e- will reduce the O_2 or H_2O in the system to $\cdot O_2^-$, and the photogenerated h^+ may oxidize the H_2O or OH^- in the system to ·OH. Through the analysis of the products after the photocatalytic oxidation reaction experiment, the anode electrode plate after the reaction was characterized to judge the treatment effect of the electrode plate and the number of repeated use. The changes of organic matter in the whole reaction process were analyzed by ultraviolet spectrophotometer and ultra-high phase liquid chromatography[17]. The generation of active substances has a great influence on the removal effect of target pollutants in the system, and the active groups that play a role in the photocatalytic oxidation and degradation of ofloxacin wastewater can be explored through the free radical quenching experiment.

5. Conclusion

In this paper, with the aim of photoelectric catalytic degradation of ofloxacin, the anode materials and experimental conditions used in the treatment process were analyzed and explored with reference to relevant literature, and its kinetics and mechanism were preliminatively analyzed, so as to explore the best degradation conditions and study its related reaction mechanism. The electrode materials were analyzed to determine the availability and recyclability of the electrode materials, and further research was carried out to obtain high catalytic performance materials for degrading antibiotics. At present, there are few studies on the coupling of photoelectric catalysis and other technologies, and the mechanism of coupling collaborative degradation of pollutants is not clear. It is possible to strengthen the research on multi-technology coupling system to improve the degradation rate and mineralization rate of antibiotics, and provide theoretical basis and support for the treatment of antibiotics in the future.

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