Degradation of Ceftriaxone Sodium in Pharmaceutical Wastewater by Photocatalytic Oxidation

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Abstract: Titanium dioxide was used as photocatalyst, UV lamp and krypton lamp after reflection were used as UV and simulated light sources respectively. The photocatalytic decomposition of ceftriaxone sodium was tracked by UV spectrum. The effects of light source, amount of catalyst, light time, electron acceptor and other ions on the decomposition of photocatalyst were investigated. The results showed that the initial concentration of mercury was 500 mg/L, and the reaction speed was 2.5g/L and 2.0 g/L, respectively, under the condition of high pressure mercury lamp and reflector lamp for 5 hours. Ceftriaxone sodium has the highest decomposition effect, 93.4% and 73.8% respectively. Adding electron acceptors to the system can promote the reaction speed of photocatalyst, and the presence of inorganic ions such as HCO_3^- SO_2^-, Cl^- can significantly reduce the activity of TiO_2 Photocatalyst. The experimental results are useful for photocatalyst treatment of antibiotic pharmaceutical wastewater.

1. Introduction

Ceftriaxone sodium, as the third generation cephalosporin antibiotic, has strong antibacterial effect, good β - lactamase tolerance, good clinical effect, low toxicity and less allergic reaction, and is widely used in clinical. Antibiotic wastewater accounts for the majority of pharmaceutical wastewater. This kind of wastewater has complex components (usually including benzene ring structure and nitrogen element), high organic matter concentration, difficult to decompose substances and barrier antibiotics, most of which are toxic, and are well known for the raw materials and process characteristics of antibiotics[1]. Moreover, nitrogen is likely to turn into nitroso compounds. Release to water is very harmful to the environment, easy to cause mutation and carcinogenesis. Therefore, the production wastewater must be treated before being discharged. At present, in order to treat the wastewater from the production of ceftriaxone sodium, biochemical decomposition method is being used. Because ceftriaxone sodium blocks or inactivates microorganisms, it can not fully play the role of decomposition, and the decomposition efficiency is low. The traditional physical and chemical treatment method is difficult to recover the adsorbent, and the cost is high, the organic matter can not be decomposed, and there are no other disadvantages[2]. It is difficult to meet the emission standards.

Photocatalyst oxidation technology has the advantages of low energy consumption (full use of solar energy), simple operation, mild reaction conditions, reduction of secondary pollution and strong oxidation ability (full inorganic organic matter). High treatment in wastewater treatment. Preferred technology. In this paper, the main pollutants in the general wastewater of biomedical products, such as ceftriaxone sodium, were selected as the photocatalytic decomposition target, and the decomposition effect of the above-mentioned refractory pollutants was studied by using the photocatalyst TiO_2 The effects of light source, electron acceptor and amount of catalyst on the reaction efficiency were investigated. No photocatalytic reaction has been reported for the decomposition of ceftriaxone sodium. It provides a theoretical basis for the application of photocatalyst technology in the decomposition of pharmaceutical wastewater.

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2. Materials and Methods

2.1. Main Reagents and Instruments

TiO_2 (Degussa P25, industrial product of Degussa company in Germany); ceftriaxone sodium for injection (Sinochem Pharmaceutical Industry CO. Ltd. in Suzhou); ammonium diferrite (yuqqiao reagent plastic company in Guangdong taixiang) KClO factory. The above reagents are analytical grade, and the experimental water is deionized water.

Ggz-125w high voltage mercury lamp (Shanghai Yaming valve factory); reflective fluorescent lamp (Nanjing Ningbao lamp); new century UV-Vis spectrophotometer (Beijing comprehensive analysis CO Ltd); glass clip thermostat atomic furnace (glass instrument factory, Sun Yatsen University); tdl-5 centrifugal separator (Shanghai anti science instrument factory)

2.2. Photocatalyst Reaction and Analysis Method

The photocatalyst experiment was carried out in a glass covered constant temperature reactor. TiO_2 (degusssa P25) was used as photocatalyst, the amount of reaction solution was 100ml, and the amount of cephalosporin sodium solution was 500mg/l. The light source is 125w mercury lamp or 250W reflection beacon lamp. The vertical distance from the liquid level is 12cm. During the reaction, the air is continuously agitated to provide the oxygen required for the reaction. Air was sampled intermittently by micro air pump[2]. After centrifugation, 4.00 ml of the upper solution is extracted every hour, and the absorbance concentration C under 0.20 ml of ferrous sulfate solutionis directly proportional to the absorbance value A. therefore, the absorbance of sample the absorbance of the sample before illumination, the absorbance of the sample at instant Tcan be obtained.

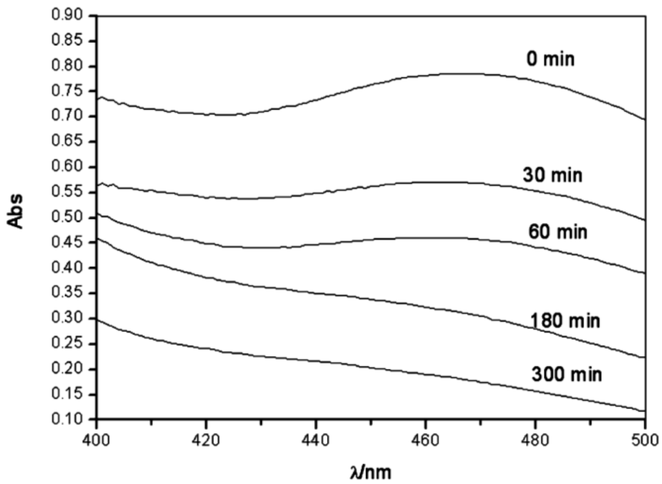

Figure 1 UV absorption spectra of ceftriaxone sodium at different reaction times

3. Results and Analysis

3.1. Photocatalytic Decomposition of TiO_2 in Ceftriaxone Sodium

When the concentration of TiO_2 photocatalyst solution was 1.0g/L under high pressure mercury lamp, the absorption peak at 470 nm disappeared and the concentration of cephalosporin sodium decreased with the time[3]. After 300 minutes, ceftriaxone sodium almost completely oxidised.

Because of the structural characteristics of cephalosporin, it is easy to hydrolyze. The powder injection preparation is stable in NaCl solution, in which the injection solution can reach 90% stability within 6 hours at 5 ℃ ~ 35 ℃[4]. The natural cephalosporin was hydrolyzed naturally and the β - lactam ring was destroyed, but the hydrolysis process was slow. On the other hand, using photocatalyst technology can speed up the decomposition of ceftriaxone sodium, greatly reduce the time in the environment, so as to reduce the harm of antibiotics left in nature to human body and environment. Decomposition products, or completely inorganic, eliminate chemical pollution.

3.2. Effect of Light Source and Catalyst Dosage

When the concentration of photocatalyst TiO_2 is 1.0, 2.0, 2.5, 3.0 g/L.

Large surface area has scattering effect on ultraviolet. When the dosage of ceftriaxone increased, the scattering degree of UV increased, the utilization rate of UV decreased, and the degradation rate of ceftriaxone also decreased. Secondly, it is difficult to disperse TiO_2 uniformly when the catalyst content is high[5]. If the catalyst agglomerates, the contact area with ceftriaxone sodium solution will be reduced, and the catalytic effect will be reduced.

Krypton lamp is a new type of gas discharge light source with high luminous efficiency, high color rendering and long life[6]. It uses charged iodine, thallium iodide, mercury and other substances to emit its unique dark spectrum. This spectrum is very close to the solar spectrum. From blue purple to orange red, the spectrum has high radiation intensity, small infrared ray and no ultraviolet ray. High concentration and light utilization. In this experiment, krypton lamp was used as the light source to simulate the sunlight, and the decomposition process and degree of cephalosporin sodium were investigated.

When the concentration of photocatalyst TiO_2 is 1.0, 2.0, 2.5 and 3.0 g/L, shows the degradation effect at this time.

When there is no catalyst under simulated sunlight, the decomposition speed of cephalosporin sodium solution is very slow and very small. After adding catalyst, the degradation rate increased significantly.

This conclusion is very important for the decomposition of ceftriaxone sodium in the environment. Generally, the absorption wavelength threshold of wide band gap semiconductors is mainly in the ultraviolet region, but almost not in the visible region[7]. The most widely used wavelength is band gap of 3.2eV, and the maximum incident wavelength of photocatalyst is 318nm, which belongs to the ultraviolet domain. The proportion of ultraviolet in sunlight is very small, so the light source used for photocatalyst is generally mercury lamp, black lamp and ultraviolet lamp. In this experiment, ceftriaxone sodium solution was used to simulate most of the decomposition in the sunlight. The use conditions of TiO_2 photocatalyst reaction expanded greatly, saving energy and making the decomposition process more green[8]. In addition, ceftriaxone sodium industrial wastewater can be decomposed. A more suitable light source is provided.

3.3. Effect of Electron Acceptor on Degradation

As a photocatalyst, TiO_2 is weak. The rate of reconnection of hole electron pairs is high, and the activity of photocatalyst is low. Therefore, one of the key to improve TiO_2 Photocatalyst is to reduce the recombination probability of positive holes and electrons. By adding strong oxidants such as KIO_3 and $KBrO_3$ to the photocatalyst reaction system, the recombination probability of the positive hole and electron generated by light can be reduced. As a good electron acceptor, these strong oxidants capture E on the surface of catalyst, weaken the recombination process of electron and positive pore, and participate in the target reaction more effectively. Due to the different ability of electron capture, the ability of oxidant to accelerate the reaction process is also significantly different. In addition, an appropriate amount of oxidants can also counteract the tendency of the reaction system to lack of oxygen, thus promoting the reactions that must be carried out in a strong oxidizing atmosphere.

$KBrO_3$ was used as electron acceptor. The electron acceptor concentration was 500 mg/L,100 ml of cephalosporin sodium solution. The electron acceptor concentration was 5 × 10 - 3 mol/L, and the catalyst concentration was 2 g/L. The photocatalytic decomposition was carried out under different light sources[9]. The effects of electron acceptors on the decomposition of ceftriaxone sodium were determined. It can be seen from that adding strong oxidant $KBrO_3$ under different light sources can increase the photocatalytic decomposition rate of cephalosporin sodium under TiO_2

Photocatalyst. It was found that the degradation rate of phenylalanine sodium in 180 minutes was the same as that without electron acceptor. This is because $KBrO_3$

4. Conclusion

TiO_2 can decompose ceftriaxone sodium and reflective bead lamp (simulating sunlight) under high pressure mercury lamp (UV) with photocatalyst. The catalytic effect of 1.0 g/l high pressure mercury lamp is better than that of reflection krypton lamp, but the use of reflection krypton lamp provides a more suitable light source for energy saving and green degradation.

The amount of titanium oxide photocatalyst will affect the decomposition efficiency of cephalosporin sodium. When the high pressure mercury lamp is used as the light source, the optimal amount of TiO_2 is 2.5G · L. when the reflector lamp is used as the light source, the optimal amount of TiO_2 is 2.0g/L.

As an electron acceptor for photocatalyst decomposition, $KBrO_3$ can reduce the recombination probability of photogenerated positive pore and photogenerated electron, and promote the photocatalyst reaction of TiO 2. By adding electron acceptors to the system, the decomposition rate of ceftriaxone sodium can be effectively increased. Under high pressure mercury lamp, the decomposition rate of ceftriaxone sodium was 2.0 g/L, the concentration of $KBrO_3$ was 5×10 - 3 mol/L, and it reached 91.7% in 180 minutes.

HCO_3^- , SO^{2-} , Cl^- and other inorganic ions can significantly reduce the activity of TiO_2 Photocatalyst. The higher the concentration of the same inorganic salt ions, the higher the deactivation of TiO_2. When the concentration of HCO_3^- is 0.05 mol/L, the decomposition rate of cephalosporin sodium is 39.7%. Therefore, in the actual treatment of pharmaceutical wastewater, these inorganic salt ions can be removed first to obtain the best catalytic effect.

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