

## Advanced oxidation processes for antibiotics removal in aqueous environment\*

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Antibiotics, as the most widely used medicine, have been detected in surface water, urban wastewater treatment plants, and soil. The distribution and degradation of antibiotics have received wide attention due to the “pseudo-persistence” and worldwide transmissions of resistance genes. Of all water treatment processes employed to degrade antibiotics, advanced oxidation processes (AOPs) based on O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, or persulfate exhibit extraordinary advantages on the rapid degradation and mineralization of various antibiotics. In this paper, several AOPs employed to degrade antibiotics including research status and applications were reviewed. Most of AOPs are pH-dependent and non-selective, thus pH and common inorganic ions in aquatic background substances have shown the significant influence on the removal efficiency of antibiotics. The characteristics of the ideal technology are proposed and the future research needs for antibiotics degradation are suggested accordingly.

**Keywords:** Antibiotics; AOPs; Degradation; pH; Inorganic Ions.

### 1. Introduction

Antibiotics have been the most important class of chemicals widely used in clinics and veterinaries. So that domestic and livestock waste-water has become main sources of antibiotics in environment. Antibiotics are regarded as “pseudo-persistent” contaminants due to their poor degradability and continual introduction into the ecosystem. Antibiotic resistance has therefore generated and transmitted rapidly, even the latest antibiotics could not avoid. Thus, antibiotics especially for the resistance induced by exposing antibiotics in aquatic environment have become a great threat to global health.

Biological and physicochemical processes are conventional methods to remove antibiotics. In these processes, antibiotics are partly degraded, and the mineralization was weaker [1]. Advanced oxidation processes (AOPs) are

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efficient methods to degrade antibiotics. AOPs apply radicals as oxidants, which can destroy the molecular structure of antibiotics directly. Meanwhile, ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ) and persulfates play important roles.

## 2. Advanced Oxidation Processes

### 2.1. Photolysis and photocatalysis

The photolysis is the decomposition or dissociation of chemical compounds caused by light. When applied in water treatment, indirect photolysis is enhanced by  $H_2O_2$ ,  $O_3$  or persulfates. The introduction of catalysts in photolysis noticeably improved the utilization of light. Researchers have made catalysts into nano particles or films to enhance performance. Besides, water-insoluble catalyst maybe a good answer for the matter of easy to coagulate and difficult to recycle.

Inversely proportional to the photon energy, the wavelengths of the light influence the removal of antibiotics apparently. Lights with shorter wavelengths seem to lead to a better removal due to its higher energy. The research of Pourakbar et al. [2] proposed that vacuum ultraviolet was an efficient and viable illuminant. In water environment or suspended matters, nature organic matter and inorganic anions would lose the removal efficiency. Considering the application of UV in disinfection, photo AOPs may be more suitable for the wastewater with low concentration of antibiotics.

### 2.2. Electrochemical oxidation

Emerged as a novel AOP, electrochemical oxidation generate  $\cdot OH$  in-situ at ambient temperature and pressure, without any addition of chemicals. Moreover, electrochemical oxidation is the most promising process to eliminate the toxicity. Antibiotics mineralization is poor when an electrochemical process is employed alone. Therefore, a long reaction time or a high current density is required. In consequence, oxidants are applied in electrochemical processes. Yao et al. [3] established an e-peroxone process, in which  $O_2$  was converted into  $H_2O_2$ , promoting the decomposition and mass transfer of  $O_3$ .

Three-dimensional (3D) electrochemical process involves particle electrodes, brings higher specific surface area and shorter mass transfer distance [4]. Despite the high current efficiency and high space-time yield, the development of 3D electrochemical process is slow due to its complication and particle electrodes' easy loss of adsorption capacity and catalytic activity.

Electrochemical oxidation is easy to operate and less affected by water quality, suitable for treatment of high concentrations antibiotic wastewater.

### 2.3. Activated persulfate oxidation

Activated persulfate oxidation has emerged as novel AOP due to its low cost and satisfactory treatment effect. Permonosulfate and peroxydisulfate are the main species of persulfate. Peroxydisulfate is applied to generate  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$ , its activator includes transition metal ions, active carbon, heat, base, UV, ultrasonic. As to the activation of permonosulphate, the categories of formed radicals rely on the activation method. Activation by metal ions generates sulfate radical, by quinone [5] generates  $^1\text{O}_2$ , a stronger oxidant than  $\cdot\text{OH}$ . At present, many novel activation methods like electrochemical and ultrasonic activation of sulfate in the laboratory study showed satisfactory treatment effect. Besides nano technology, various nano-sized iron ores are also applied.

The effluent of activated persulfate oxidation contains high concentration of  $\text{H}^+$  and  $\text{SO}_4^{2-}$ , thus advanced treatment is needed. Membrane processes show its probability to remove  $\text{SO}_4^{2-}$ . In addition,  $\text{SO}_4^{\cdot-}$  act as an electron acceptor in anaerobic bio-degradation of petroleum pollutants. Comprehensive treatment of various wastewaters maybe a promising method.

## 3. Key Factors Affecting the Removal of Antibiotics by AOPs

### 3.1. Effect of pH

The initial pH of wastewater had obviously influence on the dissociation of oxidants. As primary oxidant,  $\cdot\text{OH}$  can exist at all conditions;  $\text{SO}_4^{\cdot-}$  is stable under acidic conditions, while under alkaline condition, and it would oxidize  $\text{H}_2\text{O}$  or  $\text{OH}^-$  to generate  $\cdot\text{OH}$ . Due to the different functional groups and chemical bonds free radicals act on, the degradation rate and pathway of antibiotics owe much to pH. The morphology of the antibiotics in aqueous environment is also influenced by pH. Qiang et al. [6] investigated the degradation of sulfonamides; the removal efficiency peaked at pH 6.6-7.6, with neutral antibiotics. In practical application, water quality and cost should be considered to determine initial pH.

### 3.2. Effect of inorganic ions

$\text{Cl}^-$  in water reacts with radicals, creating chlorine radical ( $\cdot\text{Cl}$ ). Since  $\cdot\text{Cl}$  is a strong oxidant, the moderate presence of  $\text{Cl}^-$  promotes the oxidation processes. Extra  $\text{Cl}^-$  continually reacts with  $\cdot\text{Cl}$ , generating poor oxidative spiece.  $\text{HCO}_3^-$  And  $\text{CO}_3^{2-}$  have been known as the strongest radical scavengers. Nevertheless, a promotion by  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in UV/PS system was presented [7]. Different from the inhibition of  $\text{NO}_2^-$  in all the oxidation processes,  $\text{NO}_3^-$  promotes oxidation under UV irradiation, due to the generation of  $\cdot\text{OH}$ .

However, it would inhibit the processes without UV or involving oxidants [4, 7]. The inhibition mechanism of phosphates is (1) radical scavenging; (2) forming precipitate with metal ions, which covers the surface of catalyst.

#### **4. Conclusion**

AOPs are effective methods for complete degradation and removal of antibiotics in water. Considering the cost, the combination with physicochemical or biological methods is a promising trend. Moreover, the idea of comprehensive utilization should be strengthened. For example, the disinfection processes or transition metal ions in water can be applied in AOPs, thus bring about resource recovery. Meanwhile, chemicals are usually introduced in water during oxidation, claiming the intensive need for the treatment of effluents.

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