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# A Review on Advanced Treatment of Pharmaceutical Wastewater

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**Abstract.** The composition of pharmaceutical wastewater is complex, which is high concentration of organic matter, microbial toxicity, high salt, and difficult to biodegrade. After secondary treatment, there are still trace amounts of suspended solids and dissolved organic matter. To improve the quality of pharmaceutical wastewater effluent, advanced treatment is essential. In this paper, the classification of the pharmaceutical technology was introduced, and the characteristics of pharmaceutical wastewater effluent quality were summarized. The methods of advanced treatment of pharmaceutical wastewater were reviewed afterwards, which included coagulation and sedimentation, flotation, activated carbon adsorption, membrane separation, advanced oxidation processes, membrane separation and biological treatment. Meanwhile, the characteristics of each process were described.

## 1. Introduction

In China, pharmaceutical technology can be classified by productive methods. First is biopharmaceutical, which contains fermentation engineering, cell engineering, enzyme engineering and genetic engineering. The most popular is fermentation engineering. It depends on activities of microorganisms to ferment, filter and extract from organic raw materials, such as antibiotics, vitamins, amino acids. Next is chemical pharmacy, which is synthesis using multilevel chemical reactions of organic matter or inorganic matter. In addition, there is another kind of method by extracting from plants and animals or directly, called Chinese patent medicine, also known as natural medicine.

In recent years, the fast development of pharmaceutical industry has become an important part of China's national economy. In 2014, the output of chemical original medicine had reached 3.034 million tons, rose by 15.2 %, compared to the same period in 2013. There are some characteristics of the pharmaceutical industry in China, such as a multitude of enterprises and products with small scale, scattered overall arrangement. By the end of 2014, the pharmaceutical enterprises have reached 7108 in China, which was 8.9 % higher than 2013. Only 1609 among them are large or medium-sized enterprises.

However, with the development of pharmaceutical industry, the environmental pollution is becoming more and more serious. Due to the variety of the pharmaceutical industry products, and the difference of production scale and process, there are many kinds of pharmaceutical wastewater. Biopharmaceutical wastewater is mainly generated by high-concentrated antibiotic wastewater, which is characterized as strong fluctuation in quantity, low C/N, high SS concentration, high sulfate concentration, complicated composition, biological toxicity and high chroma. The composition of



chemical pharmacy is single, leading to lack of nutrition. It also has high concentration and salt content. And it is hard to biodegrade and toxicity to microbiology [1].

Along with the strict government standard, traditional treatment methods of pharmaceutical wastewater are difficult to satisfy the demand. Therefore, advanced treatment of pharmaceutical wastewater is essential.

The review aims to introduce the fundamental advanced treatment of pharmaceutical wastewater.

## 2. Characteristics of pharmaceutical wastewater

### 2.1. Characteristics of pharmaceutical wastewater

In general, the composition of pharmaceutical wastewater is complex, which has high concentration of organic matter, microbial toxicity, high salt, and it's hard to biodegrade [2,3]. In addition, most of pharmaceutical factories are batch process, and there are different raw materials and production process, which causes huge varieties in different wastewater [4]. Table1 provided a summary of the characteristics of pharmaceutical wastewater [5].

**Table 1.** Common pharmaceutical wastewater physicochemical properties

COD (mg/L)	BOD <sub>5</sub> (mg/L)	TN (mg/L)	TP (mg/L)	SS (mg/L)	Chromaticity (times)	Temp. (°C)	pH
1000-10000	500-2500	500-1500	50-250	200-500	500-1000	25-80	1-8

Otherwise, different kinds of pharmaceutical wastewater has different characteristics. Biopharmaceutical wastewater is characterized as strong fluctuation in quantity, low C/N, high SS concentration, high sulfate concentration, complicated composition, biological toxicity and high chroma. Chemical pharmacy is lack of nutrition, hard to biodegrade and toxicity to microbiology, and it also has high salt content. The characteristics of the wastewater of Chinese patent medicine is containing sugar, glycosides, organic pigment, anthraquinone, tannins, Alkali content, cellulose, lignin and other organic matter [6].

### 2.2. Characteristic of secondary effluent

Biological treatment is mainstream for pharmaceutical wastewater at home and abroad, which is the most economical way to remove organic pollutants. Therefore, organic matter are the main pollutants in pharmaceutical wastewater. Biological treatment technologies can be generally divided into aerobic process, anaerobic process and combination of anaerobic-aerobic process [7]. After secondary treatment, almost every kind of pollutants concentration are decline.

However, due to their own complex features of pharmaceutical wastewater, and discharge standard is increasingly strict, the current methods are hard to satisfy the demand.

## 3. Methods of Advanced treatment of pharmaceutical wastewater

In recent years, the main emphasis of the scientific research and engineering application has shifted to advanced treatment of pharmaceutical wastewater, which main method is physicochemical technology [7]. It means that wastewater is treated by physical or chemical methods, like coagulation and sedimentation, flotation, activated carbon adsorption, advanced oxidation processes, membrane separation.

### 3.1. Coagulation and sedimentation

Coagulation is adding chemical agents to wastewater, dispersing by rapid mixing, then making stable pollutants into unstable and precipitable matters. The mechanism of coagulating is complex. For advanced treatment of pharmaceutical wastewater, the key is how to squeeze and remove bound water round hydrophilic colloid. So the character of flocculent is important, which related to the effect of coagulation. Inorganic metal salts and polymers are frequently used as flocculent. This method can remove SS, chromaticity and toxic organic matter [8]. Meanwhile, it can improve the biodegradability of pharmaceutical wastewater.

Sedimentation is the most common method after coagulation. Under the gravity, pollutants can be separated, which has greater density than wastewater.

Coagulation and sedimentation have some advantages, such as easy operation and mature technology, but it is hard to remove dissolved organic matter.

### 3.2. Flotation

Except for sedimentation, flotation can also remove suspended solids of secondary effluent. The technology characteristic is producing a large number of tiny bubbles by injecting air into wastewater, forming floating floc with smaller density than wastewater. And it can float to the surface of wastewater to separate.

### 3.3. Activated carbon adsorption

Activated carbon, as a kind of adsorbent, has many advantages. It has large specific surface area, multilevel pore structure, high adsorption capacity and stable chemical property. Therefore, it is widely used as adsorbent or catalyst carrier to remove pollutants [9,10]. In industrial effluents treatment, activated carbon is used for effluent, which is toxic and hard to achieve discharge standard. It is an important method of advanced treatment of pharmaceutical wastewater as well.

Activated carbon adsorption can be classified as physical adsorption and chemical adsorption. Physical adsorption is reversible, and no selectivity to adsorbate. When activated carbon saturated by adsorbates, it is easy to desorb. To the contrary, chemical adsorption adsorbs only one or several specific adsorbates, which is irreversible and hard to desorption. For cyclic utilization, saturation of activated carbon restores its adsorption property by regeneration.

This method is widely used for advanced treatment, because it can be recycled, its better treatment effect and wide suitability. But there are some disadvantages, such as high costs relatively, low efficiency of regeneration and complex operation, which limit application.

### 3.4. Advanced oxidation processes

Advanced oxidation processes (AOPs), which can oxidize pollutants by forming free radicals. Those kinds of pollutants cannot be degraded by common oxidizing agent. There are many kinds of AOPs, such as wet air oxidation, supercritical water oxidation, Fenton reagent, photocatalytic oxidation, ultrasound oxidation, electrochemical oxidation and ozonation.

**3.4.1. Wet air oxidation(WAO).** WAO has been put forward by F. J. Zimmer Mann in 1958, which was used for papermaking black liquid treatment. By using of air or oxygen as the oxidant, this method decomposes organic matter into inorganic or small molecules at high temperature (150-350 °C) and high pressure (0.5-20 Mpa). WAO is generally used in pretreatment of wastewater advanced treatment.

This method has wide range of applications, high efficiency of COD removal, which can even reaches more than 90 % under appropriate conditions, low energy consumption, less secondary pollution, and it is easy management.

**3.4.2. Supercritical water oxidation(SCWO).** SCWO is chemical reaction between dissolved oxygen and organic pollutants in supercritical water. Organic matter, air, and supercritical water were complete mixed at 24 Mpa pressure and 400 °C temperature, becoming homogeneous phase. Under these conditions, organic compounds spontaneously initiate the oxidation reaction. With the increase of the reaction temperature, 99.9 % or more of the organic matter is rapidly oxidized into simple non-toxic small molecules in a period of time, achieving the purpose of removing pollutants.

SCWO has high oxidation efficiency, will not cause secondary pollution, organic can be oxidized completely. However, this method has some shortcomings, such as it requires high operating conditions and high cost.

**3.4.3. Fenton reagent.** Fenton system was initially used in organic synthesis, with the deepening of people's understanding of it, the system was gradually applied to industrial wastewater treatment.

Fenton reaction can be carried out under normal temperature and pressure, and less damage to the environment [11]. It is an advanced oxidation method, which is simple, mild reaction conditions, and high oxidation efficiency. However, the shortcomings of the Fenton reaction cannot be ignored. One is due to free radical scavenging and decomposition of  $\text{H}_2\text{O}_2$  itself, leading the loss of oxidant. The other is the formation of iron mud in the neutral conditions, making it hard to the subsequent processing [12].

**3.4.4. Photocatalytic oxidation.** Photochemical oxidation, also known as ultraviolet photocatalytic oxidation, is a method combination of UV radiation and oxidant. In the excitation of ultraviolet light, oxidative decomposition of oxidants produces stronger oxidative capacity of free radicals, which can oxidize more difficult to decomposition of refractory organic pollutants with oxidants only.

According to the types of oxidants, photochemical oxidation can be divided into UV /  $\text{O}_3$ , UV /  $\text{H}_2\text{O}$ , UV /  $\text{H}_2\text{O}_2$  /  $\text{O}_3$  and so on. At present, the steps of the reaction process still can't be described. However, the effect of this method on the treatment of refractory organic matter is undeniable.

**3.4.5. Ultrasound oxidation.** Ultrasonic degradation of organic matter in wastewater is a physical and chemical degradation process, mainly based on ultrasonic cavitation effect and the resulting physical and chemical changes, which includes the following three ways: free radical oxidation, pyrolysis and supercritical water oxidation.

There are many factors that affect the effect of ultrasonic degradation of organic pollutants in wastewater. The main factors are ultrasound frequency, sound power, ultrasonic time, solution temperature and pH, and the nature of organic matter.

**3.4.6. Electrochemical oxidation.** The use of electrochemical reaction to remove toxic and harmful pollutants in the water, is known as the electrochemical method. Electrochemistry is a new method in water treatment field. The principle of the method is as follow: in the electrochemical reaction process, the reactant will lost electrons and be oxidized in the anode. Conversely, the reactant in the cathode will lose electrons and be reduced. In general, the removal of refractory organic matter, mainly due to the oxidation of the anode. Conventional electrochemical wastewater treatment processes includes: electrolytic recovery, electrochemical oxidation, electrolytic air flotation, electrodialysis and micro-electrolysis.

Electrochemical method is also known as "Environmentally Friendly" process, has a great advantage compared with other methods. For example, the electrochemical method is generally carried out under normal temperature and pressure and has high efficiency, can be used alone or in combination with other processes, and it covers a small area and no secondary pollution, has relatively high degree of automation. The main research direction of the electrochemical reaction in the future is the research of the anode and electrochemical reactor [13].

**3.4.7. Ozonation.** For a long time, ozone is considered to be a very effective oxidant and disinfectant. In acidic conditions, ozone is primarily an oxidant. But in neutral and alkaline conditions, it mainly relays on free radical reactions. Table 2 shows the oxidation potential of various oxidants. It can be seen that the oxidation capacity of ozone is significantly higher than other conventional oxidants.

**Table 2.** The oxidation potential of various oxidants

Oxidant	Half-reaction	Oxidation potential(V)
$\bullet\text{OH}$	$\bullet\text{OH} + \text{H}^+ + \text{e} \rightarrow \text{H}_2\text{O}$	3.06
$\text{O}_3$	$\text{O}_3 + 2\text{H}^+ + 2\text{e} \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.07
$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O}$	1.77
$\text{HClO}$	$2\text{HClO} + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{Cl}^- + 2\text{H}_2\text{O}$	1.63
$\text{Cl}_2$	$\text{Cl}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{Cl}^-$	1.36

Ozone can quickly oxidize and decompose most of the organic matter in the water, which can effectively remove pollutants in water. However, it is difficult to directly mineralize. Instead, a product which is easily biodegradable can be produced. At the same time, it can also effectively remove turbidity and pathogens in wastewater.

Ozone can be combined with other wastewater treatment technologies, forming ozone advanced oxidation technology. This method has stronger oxidation ability and lower selectivity to reactants. Such as  $O_3 / H_2O_2$ ,  $O_3 / UV$ , etc.

### 3.5. Membrane separation

Under certain driving force across the membrane, a component in water selectively permeates it by using permselective membrane separating media, which is called membrane separation. In this way, achieve the separation, purification, concentration of the target substance from the mixture. There are several membrane separation techniques in wastewater treatment. Such as microfiltration, ultrafiltration, reverse osmosis and electrodialysis.

**3.5.1. Microfiltration(MF).** MF is based on static pressure as the driving force, and the separation process is performed by the action of the sieve separation of the membrane, which principle is similar to traditional filtration. The slight difference is that the pore size of MF is smaller. This method can effectively remove SS and microorganisms in wastewater.

**3.5.2. Ultrafiltration(UF).** UF driving force is the pressure difference between the membranes on both sides, the filter medium is the ultrafiltration membrane. Under certain pressure, when water passes through the membrane surface, water, inorganic salts and small molecules penetrate, other macromolecules are trapped.

This method is mainly used for the removal of macromolecules and colloids in wastewater. In the application of this method, it should be ensured that the membrane has adequate membrane flux and is easily disassembled, replaced, cleaned.

**3.5.3. Reverse osmosis(RO).** There are two categories of RO membrane, cellulose ester and aromatic polyamide. Its component form includes tube, plate and frame, roll and hollow fiber type.

RO process can remove a wide range of impurities, dissolved inorganic salts and a variety of organic matter. Meanwhile, it has a high efficiency of salt removal and water reuse rate. However, this method requires a high pretreatment of the feed water. With the development of RO, nanofiltration (NF) has been proposed as a new method.

**3.5.4. Electrodialysis(ED).** ED is a combination of electrolytic and dialysis diffusion process. Under the action of the DC electric field, anions and cations of the dissolved salts in the wastewater are moved to the anode and the cathode respectively. In this way, the concentration of anions and cations in the intermediate compartment is gradually reduced, and the separation and recovery are achieved.

This method has many advantages, such as less energy and pharmaceutical consumption, less environmental pollution, easy to operate and automate. But it can only remove the salt in water, and desalination efficiency is lower than RO.

### 3.6. Biological treatment

In theory, after secondary treatment, pharmaceutical wastewater should not be treated by biological methods, because of its poor biodegradability. However, we cannot ignore the advantages of biological treatment, such as low cost, stable treatment effect. It can be used as a way of pretreatment in advanced treatment.



#### 4. Conclusion

Due to the complexity of pharmaceutical processes, pharmaceutical wastewater has some characteristics, such as poor biodegradability and high concentration. From these characteristics, advanced treatment of pharmaceutical wastewater is very necessary. There are many kinds of advanced treatment, each method has its own features. Through rational utilization of various methods, can effectively improve the quality of pharmaceutical wastewater effluent.

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