Application and Improvement of Wet Oxidation Technology

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Abstract. The common treatment methods for industrial biodegradable industrial waste-water are physical, chemical and biological methods, but the conventional methods have complicated and inefficient treatment processes. Wet Air Oxidation (WAO) technology can effectively treat industrial biodegradable industrial waste-water. WAO has achieved good results in the treatment of pesticide waste-water, dye waste-water, activated sludge and phenol-containing waste-water. The CODCr removal rate of waste-water reaches 72.3 %~95.3 %. In order to further improve the application effect of WAO technology, three improvement approaches have been developed: Catalytic Wet Air Oxidation, Catalytic Wet Supercritical Oxidation, and Catalytic Wet Peroxide Oxidation.

1. Introduction
With the progress of society, the amount of industrial waste-water that is difficult to biodegrade is increasing, which constitutes an important source of water environmental pollution [1]. The traditional physical method (filtration method, precipitation method, adsorption method, air floatation method), chemical method (chemical coagulation method, electrochemical method, oxidation method) and biological method are used to treat industrial waste-water. The treatment process is complicated and the equipment occupies a large area and the treatment efficiency is low [2-3], and Wet Air Oxidation is an advantageous way to treat printing and dyeing waste-water. Wet Air Oxidation (WAO) technology is an advanced oxidation technology for the treatment of high-concentration organic waste-water developed in recent decades. It is a chemical process that oxidizes and decomposes organic pollutants into carbon dioxide and water and other inorganic substances or small organic molecules under the conditions of high temperature (125 ~ 320 °C) and high pressure (0.5-20 MPa) [4]. Scholars at home and abroad have conducted some research on WAO technology, and have made certain research results in terms of process equipment and catalyst preparation [5-6].

2. Application of wet oxidation technology

2.1. Application Overview
At present, the application of the wet oxidation method is mainly divided into WAO aspects: one is for the pretreatment of high-concentration and difficult-to-degrade organic waste-water for biochemical treatment to improve biodegradability; the other is for the treatment of toxic and harmful industrial waste-water. The application overview of WA technology is shown in Table 1.
Table 1. Application overview of WAO technology.

| No | Processing object          | Processing effect                                                                 | Cases          |
|----|-----------------------------|-----------------------------------------------------------------------------------|----------------|
| 1  | Pesticide waste-water       | The COD$_{Cr}$ removal rate of raw water COD$_{Cr}$ 110'0000 mg/L reached 95.3% | [7]            |
| 2  | Dye Waste-water             | The COD$_{Cr}$ of the waste-water was 2000 mg/L. At a reaction temperature of 180 °C, an oxygen partial pressure of 1.0 MPa, and a pH of 5.25 in the feed water for 150 minutes, the COD$_{Cr}$ removal and decolorization rates reached 83.6% and 98.3%, respectively. | [8-9]         |
| 3  | Activated sludge            | At a temperature of 200 °C and an oxygen partial pressure of 0.8 MPa, the degradation rate reached 72.3% by WAO technology for 60 minutes. | [10-11]        |
| 4  | Phenolic waste-water        | The COD$_{Cr}$ of the phenol-containing waste-water is 9300 mg/L, and it is oxidized for 0.58 h at a temperature of 180-250 °C and an oxygen partial pressure of 0.98-3.43 MPa, and the COD$_{Cr}$ removal rate is higher than 88.0%. | [12-16]        |

2.2. Treatment of pesticide waste-water
China's pesticide consumption is quite large. According to incomplete statistics, China produces more than 100 kinds of pesticides, including pesticides and herbicides, with an annual output of more than 200,000 tons. Among them are: organophosphorus pesticides. Pesticide waste-water has the following characteristics: ① small amount of water; ② high concentration (COD above 5000 mg/L); ③ large changes in water quality; ④ complex components and high toxicity. Most of the domestic treatment methods for pesticide waste-water are biochemical treatment after pretreatment, and common pretreatment methods include alkali hydrolysis, acid hydrolysis, precipitation extraction and solvent extraction. These technologies can theoretically decompose or separate toxic components in pesticides into non-toxic products, but in actual applications, current treatment technologies cannot completely decompose or separate toxic components in waste-water, and high dilutions are required to reduce toxicity before entering biochemical treatment, so the pretreatment is of little significance. In addition, it also increases the load of the biochemical method, and at the same time, the amount of medicine and the operating cost also increase. The wet oxidation method can achieve better treatment results [7], and the results are shown in Table 2:

Table 2. Treatment effect of pesticide and herbicide waste-water with WAO.

| Waste-water                  | Process conditions | Pollutant       | Water (mg/L) | Effluent (mg/L) | Removal rate (%) |
|------------------------------|--------------------|-----------------|--------------|-----------------|------------------|
| Pesticide waste-water from Michigan Chemical Corporation | Temperature: 281 °C Time: 182 minutes Water volume: 54.5 m$^3$/h | COD$_{Cr}$, DOC, Dinol, Malathion | 110'000, 26'600, 57.1, 93.1 | 52'00, 10'10, 0.186, 0.130 | 95.3, 96.0, 99.5, 99.9 |
| Herbicide Waste-water from Michigan | Temperature: 245 °C Time: 60 minutes | COD, Herbicide by-products | 78'200, 735 | 34'200, 5-13.3 | 55.0, 98.2-99.3 |

2.3. Treatment of dye waste-water
China's dye industry is developed, and its output accounts for one fifth of the world's total output. The pollutants contained in the dye waste-water include amino compounds, nitro compounds, amines,
sulfonates, halides, etc., with benzene, phenol, naphthalene, anthracene, quinone as the parent. These substances are mostly polar, easily soluble in water, complex in composition, high in concentration, and highly toxic. The COD$_{Cr}$ values are generally above 5000 mg/L, even as high as 75,000 mg/L. In recent years, the new dyes are all anti-oxidation and anti-biodegradation, and the treatment is increasingly difficult. The general physicochemical and biological methods are difficult to handle, and the effluent cannot meet the discharge requirements. Wet oxidation technology can effectively degrade toxic components in dye waste-water, decompose organic matter, and improve biodegradability of waste-water [8-9].

2.4. Treatment of activated sludge
After biological treatment of waste-water, a large amount of activated sludge was produced. The usual method is to dehydrate the activated sludge through a drying bed or vacuum filtration, and then landfill or incineration. The landfill method will cause new pollution problems and require a large area for sludge recovery; the incineration method requires a large amount of energy consumption and high cost. The WAO technology can oxidize activated sludge into a form that is sterile, biologically stable, and convenient for landfill and dehydration, and the amount of sludge is greatly reduced, and the treatment cost is significantly reduced. Quitain et al. [10] used sewage sludge, fish offal and other high protein sludge and paper mill sludge with high cellulose content as research objects. Under the conditions of 623 K and 16.5 MPa total pressure, wet oxidation for 30 minutes, the main products obtained are small molecule organic acids such as acetic acid, formic acid, propionic acid, succinic acid and lactic acid, of which acetic acid accounts for 90%. Lactic acid is an important raw material substance, which has important practical value and can be recycled. Yang Xiaoyi et al. [11] studied chemical waste-water, oil refining waste-water, and municipal sewage residual sludge. At a temperature of 200 °C and an oxygen partial pressure of 0.8 MPa, wet oxidation for 60 minutes, the degradation rates were 67.4%, 70.4%, 72.3%; The BOD$_5$/COD$_{Cr}$ values of the wet oxidation supernatant were 0.51, 0.51, and 0.52, respectively. The biodegradability was good.

2.5. Treatment of phenolic waste-water
Phenol-containing waste-water comes from a wide range of sources, such as coking waste-water, coal gasification waste-water, petrochemical waste-water, polymer material production waste-water, and pharmaceutical, pesticide and other industries also produce a large number of high-concentration phenol-containing waste-water. The maximum allowable concentration of phenol in water bodies specified by general national standards is extremely low (China's drinking water bodies ≤ 0.002 mg/L), so the treatment of phenol-containing waste-water is a topic of universal importance. At present, there are various problems with traditional treatment technologies: the extraction method is difficult to meet the standard and the solvent consumption is large; the adsorption method requires a high degree of pretreatment, and the adsorbent is expensive; the chemical oxidation method has a good treatment effect while the oxidant cost is high. In contrast, the wet oxidation treatment of phenol-containing waste-water has a better application prospect: the effluent treatment effect is stable, the biodegradability is good, and it can be directly discharged after treatment at a relatively low influent concentration; if the influent concentration is extremely high, it can be complemented by biochemical methods. Zhang Qiubo et al. [12] treated the phenol-containing waste-water with a COD$_{Cr}$ of 9.3 g/L in the feed water, oxidized for 0.58 h at a temperature of 180-250 °C and an oxygen partial pressure of 0.98-3.43 MPa, and the COD$_{Cr}$ removal rate exceeded 88.0%; Tang Shouyin et al. [13] treated the phenol-containing waste water with a COD$_{Cr}$ of 7.8-8.7 g/L, and oxidized for 0.5 h at a temperature of 150~250 °C and an oxygen partial pressure of 0.7~5.0 MPa, and the COD$_{Cr}$ removal rate reached 52.9%-90%.

In addition, WAO technology is also used in the treatment of emulsion waste-water, activated carbon regeneration [14], and oxidative desulfurization of coal [15]. Tang et al. [16] treated the emulsion waste-water with a COD$_{Cr}$ of 48 g/L at 220 °C and an actual oxygen partial pressure of 1.25 times the theoretical oxygen partial pressure. After 120 minutes of reaction, the COD$_{Cr}$ removal rate of
the waste-water reached 86.4%. WAO generates heat during the oxidation of organics, and this energy can be used to generate steam. The advantage of WAO production capacity is that it does not produce N and S compounds that pollute the atmosphere, and the efficiency of energy recovery at the WAO technology plant is higher than that of traditional coal combustion furnaces.

3. Improved ways of wet oxidation technology

3.1. Overview of improved technologies

Because of the above-mentioned shortcomings of WAO technology, it is the focus of research at home and abroad to improve the traditional wet oxidation process, reduce its reaction temperature and pressure, and promote its completeness. There are three main ways of improvement, which are summarized in Table 3.

| No. | Ways to improve                  | Technical principle                                                                                                                                                                                                 | Cases       |
|-----|----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1   | Catalytic Wet Air Oxidation      | Adding a catalyst to the WAO reaction system reduces the reaction activation energy, thereby reducing the temperature and pressure of the reaction system and improving the effect of waste-water treatment.                                      | [17-23]     |
| 2   | Catalytic Wet Supercritical Oxidation | For wet air oxidation technology, when the reaction temperature and pressure exceed the critical point of the medium, it is called supercritical oxidation technology. Compared with WAO, CWSO can further improve the treatment effect of waste-water. | [24-28]     |
| 3   | Catalytic Wet Peroxide Oxidation | In the WAO reaction system, liquid oxidant H₂O₂ is used instead of O₂. Therefore, at higher temperatures, the pressure is slightly higher than the saturated vapor pressure of water (to maintain the liquid phase reaction), thereby improving the reaction effect. | [29-32]     |

3.2. Catalytic Wet Air Oxidation

From the short-term goals of the project, catalytic wet oxidation technology is the most valued part. In this respect, Japan and some European and American countries have done more research [17-19]. Catalytic reactions can be divided into two types: homogeneous and heterogeneous: homogeneous catalysis refers to a catalytic reaction in which the catalyst and reactants are in the same phase, usually a liquid phase reaction. In homogeneous CWAO, the catalyst is in full contact with the waste-water, and the treatment efficiency is high, but the catalyst is easy to lose, causing economic losses and secondary pollution to the environment. Generally, subsequent treatment is required to recover the catalyst in the effluent [20]; heterogeneous Catalysis refers to reactions in which the reactants and the catalyst are in different phase states, usually a solid-liquid phase reaction or a solid-gas phase reaction, that is, the catalyst is a solid phase and the reactants are a liquid phase or a gas phase. In heterogeneous CWAO, the separation of catalyst and waste-water is simple, which greatly simplifies the treatment process. Since heterogeneous catalysts have the advantages of high activity, easy separation, and good stability, after the 1970s, researchers turned their attention to the development of efficient and stable heterogeneous catalysts [21-23].

3.3. Catalytic Wet Supercritical Oxidation Technology, namely CWSO Technology (Catalytic Wet Supercritical Oxidation)

For wet oxidation technology, when the reaction temperature and pressure exceed the critical point of the medium, it is called supercritical oxidation technology. This technique was proposed in the 1980s by Modell [24] in the United States. In addition to solids, liquids, and gases, supercritical fluids, which can be referred to as the fourth state of matter, have been discovered. The so-called supercritical fluid refers to the special fluid state in which the temperature and pressure of a substance are higher than its
inherent critical temperature and pressure, respectively. When the substance in gas-liquid equilibrium is heated and pressurized, thermal expansion causes the density of the liquid to decrease, and the increase in pressure causes the density of the gas to increase. When the temperature and pressure reach a certain point, the gas-liquid phase interface disappears, and this point is the critical point, at which time matter becomes a homogeneous system. Supercritical fluid not only has the density, dissolving ability and good fluidity of similar liquid, but also has the diffusion coefficient and low viscosity of similar gas. The fluid cannot be liquefied no matter how compressed it is under pressure, so the supercritical fluid can be simply called an intermediate state between liquid and gas, which can be called "heavy gas" and "very loose liquid". It has many unique physical and chemical properties.

Kuen-Song et al. [25] investigated the removal of 2-chlorophenol by CuO/ZSM-5 in a supercritical state, and showed that 2-chlorophenol was well treated, and only trace amounts of polymers existed in the reaction out of the water. Ding et al. [26] introduced a MnO2/CeO2 catalyst in the supercritical water oxidation of ammonia, which greatly improved the conversion rate of ammonia, and the excess oxygen enhanced the reproducibility of the active site of the catalyst. Johnson [27] and Thomason [28] used CWSO technology to treat biochemical pharmaceutical waste-water and various harmful compounds respectively, and achieved good results.

3.4. Catalytic Wet Peroxide Oxidation Technology, namely CWPO Technology (Catalytic Wet Peroxide Oxidation)

It is the wet oxidation treatment technology using hydrogen peroxide as an oxidant [29-30]. There are two parts to the total pressure of the WAO system, one is the saturated vapor pressure of water at this temperature, and the other is the initial partial pressure of oxygen required under the reaction conditions. To reduce the total reaction pressure of the system, an effective way under high temperature reaction conditions is to eliminate gaseous oxygen and replace it with liquid oxidant. On the one hand, the addition of liquid oxidant H2O2 replaced high-pressure oxygen or compressed air, thereby saving a lot of high-pressure power equipment or air separation equipment, reducing the total pressure of the system, thereby overcoming equipment corrosion and operational safety issues caused by high pressure in the wet oxidation process. On the other hand, the liquid oxidant H2O2 replaces the gaseous oxidant, overcomes the resistance of gas-liquid mass transfer, and thus speeds up the reaction. Therefore, the use of liquid oxidant H2O2, at a higher temperature, the pressure is slightly higher than the saturated vapor pressure of water (to maintain the liquid phase reaction), thereby improving the reaction effect. Tian Jinjun et al. [31] used CWPO technology to treat sodium sulfide waste lye. After 120 minutes, the removal rate of sodium sulfide reached more than 99 %. Ke Ding et al. [32] used CWPO technology to treat ethyl acetocacetate waste-water. At 90 °C, the dosage of Fe2+ and H2O2 were 10 mg/L and 31.5 mg/L, after 150 minutes reaction, the COD Cr removal rate of the waste-water could reach 98.5 % or more.

4. Conclusion

Physical method, chemical method and biological method are common treatment methods for difficultly biodegradable industrial waste-water. However, the treatment process of these methods is complicated and the treatment efficiency is low. Wet oxidation technology can effectively treat difficultly biodegradable industrial waste-water. For pesticide waste-water, dye waste-water, activated sludge and phenol-containing waste-water, WAO technology has achieved good results in treatment, and the COD Cr removal rate of waste-water reaches 72.3 %~95.3 %. There are three ways to improve the developed WAO technology: Catalytic Wet Air Oxidation, Catalytic Wet Supercritical Oxidation, and Catalytic Wet Peroxide Oxidation, which can further improve the application effect of WAO technology.
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