Study on the treatment of actual waste-water by CWAO method

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Abstract. The use of catalytic wet air oxidation (CWAO) technology to treat organic waste-water that is difficult to biodegrade had a significant effect. The following 12 types of waste-water have achieved good results with the CWAO method. The 12 types of waste-water include: papermaking waste-water, dye waste-water, pesticide waste-water, perfume waste-water, phenol waste-water, carbon-containing waste-water, ethanol waste-water, petrochemical company alkali residue waste-water, and oil extraction waste-water, ammonia-containing coking waste-water and pesticide waste-water, cleaning workshop emulsified waste-water and desizing waste-water. A typical homogeneous catalytic wet oxidation system includes 5 processes: Ciba Geigy, Bayer Loprox, WPO, Orcan, and IT Envirosience. Heterogeneous catalysts lose their activity due to the low pH of the reaction system and the accumulation of activated carbon.

1. Introduction
Wet air oxidation technology (WAO), which uses pure oxygen or oxygen in the air as an oxidant, is a chemical process that oxidizes organic pollutants into inorganic or small molecular organic substances in the liquid phase under high temperature (125~320 °C) and high pressure (0.5~20 MPa) conditions [1]. This technology was proposed by Zimmermann in 1944, and WAO was used for the first time to treat papermaking black liquor waste-water in 1958. The COD removal rate of waste-water reached 90 % [2-3]. When WAO oxidizes organic pollutants, the organic nitrogen is oxidized to NH$_3$, NO$_3^-$ and N$_2$, and the halides and sulfides are oxidized to the corresponding baseless halides and sulfides. During the reaction process, no harmful substances such as NO$_x$, SO$_2$, HCl and CO are generated, secondary pollution is small, and energy and useful materials can be recovered. This is a promising water treatment method, so it has received extensive attention from scientific researchers around the world. Although WAO is an effective technology for treating high-concentration, toxic, harmful, and biologically difficult to degrade organic waste-water, it is difficult to achieve large-scale applications due to the relatively harsh conditions required by the technology. Therefore, since the 1970s, a series of new technologies have been developed on the basis of WAO, such as Catalytic Wet Oxidation (CWAO) using efficient and stable catalysts. According to the different oxidants, CWAO (Catalytic Wet Air Oxidation) technology can be divided into CWAO technology using air or oxygen as oxidant and CWPO (Catalytic Wet Peroxide Oxidation) technology using peroxide as oxidant [4].
At present, the study of using CWAO technology to treat refractory organic pollutants has received widespread attention. By adding appropriate catalyst and oxidant, this technology enables the oxidant to be rapidly decomposed into free radicals with strong oxidizing capacity under the action of the catalyst, thus speeding up the reaction speed and reducing the activation energy of the reaction. The key to CWAO technology is the research and development of efficient and stable catalysts [5]. Compared with traditional WAO technology, CWAO technology reduces the temperature and pressure required for the reaction to a certain extent. Therefore, it is favored by more and more researchers.

2. Case analysis of CWAO method for treating actual waste-water

CWAO technology makes the reaction conditions more mild and improves the degradation efficiency of organic matter. There are many reports on CWAO technology for treating simulated waste-water, but relatively few reports on actual waste-water treatment. They are summarized in Table 1:

| No. | Cases | Treatment | catalyst | Processing effect |
|-----|-------|-----------|----------|-------------------|
| 1   | [6-7] | Papermaking waste-water | Cu, Mn, Pd and Cu/Pd, Mn/Pd, Cu/Mn composite catalyst | It is found that the composite catalyst was more effective than the single-component catalyst. Under the conditions of 463 K, an oxygen partial pressure of 0.74 MPa, and an inlet pH of 11.3, the removal rate of TOC was 78.8 % for Cu/Pd series and 74.1 % for Mn/Pd series and 57.8 % for Cu/Mn series. |
| 2   | [8-9] | Dye waste-water | CuSO₄ | Under conditions of 498 K and oxygen partial pressure of 0.69–1.38 MPa, the CODₜₜₜ removal rate reached 90%. |
| 3   | [10] | Pesticide waste-water | Cu/η-Al₂O₃ | When the water-soluble nitrogen-containing dye X-3B waste-water was treated, the CODₜₜₜ degradation rate and decolorization rate of the waste-water were 77 % and 99 % at 120 minutes, respectively. |
| 4   | [11] | Perfume waste-water | ABO₃, rare earth catalyst | Under the conditions of 433 K and an oxygen partial pressure of 0.98 MPa, the removal rates of CODₜₜₜ, TOC, and chroma reached 30.1 %, 74.8 %, and 79.5 % at 30 minutes, respectively. |
| 5   | [12] | Phenol waste-water | Cu/η-Al₂O₃ | At 413 K and a certain air pressure (3 times the theoretical oxygen demand), the CODₜₜₜ removal rate reached 93.2 % and BODₐ/CODₜₜₜ reached 0.5. |
| 6   | [13] | Carbonaceous waste-water | Pt/γ-Al₂O₃ | At 435 K for 30 minutes, the glucose degradation rate reached 70 %. |
| 7   | [14] | Ethanol waste-water | Pt/Al₂O₃, Mn/CoOₓ, Cu(II)/Zeolite | Under conditions of 453-532 K and oxygen partial pressure of 0.5-2.5 MPa, the degradation rate of TOC using Mn/CoOₓ and Cu(II)/zeolite is higher than that of Pt/Al₂O₃. |
| 8   | [15] | Alkali residue waste-water from petrochemical company | Alloy catalyst | Under the conditions of 503 K and air pressure of 6.6 MPa, the CODₜₜₜ removal rate reached 78 %, the sulfur removal rate reached 99 %, and the BODₐ/CODₜₜₜ exceeded 0.8. |
| 9   | [16] | Production waste-water | Copper-laden activated carbon | Contacting the catalyst at 290-308 K and atmospheric pressure for 120 minutes can reduce the CODₜₜₜ in the oil production waste-water, which is 45 times the volume of the catalyst, from 0.4 kg/m³ to 0.1 kg/m³. |
| 10  | [17] | Ammonia-containing coking waste-water and pesticide waste-water | Ru-Ce/TiO₂ | The CODₜₜₜ and ammonia removal rate of the solution reached 99.6 %, which reached the national emission standard, and the catalyst had good resistance to acid and alkali. |
| 11  | [18] | Emulsified waste-water from cleaning workshop | Cu/γ-Al₂O₃ | Under the conditions of 473 K and an oxygen partial pressure of 1.2 MPa for 120 minutes, the CODₜₜₜ removal rate reached 89.5 % and the TOC removal rate reached 81.7 %. |
| 12  | [19] | Desizing waste-water | CuSO₄ | At 200 °C and air pressure of 10 MPa for 60 minutes, the CODₜₜₜ removal rate reached 80 %. |
3. Application of CWAO technology in industrial water treatment

At present, CWAO technology has become the focus of research at home and abroad, but its industrial application has great limitations, which are limited to coking waste-water and chemical waste-water treatment.

In recent years, some typical homogeneous catalytic wet oxidation systems have been developed abroad [20], as shown in Table 2.

**Table 2. Typical homogeneous catalytic wet oxidation systems.**

| No. | system name          | System Overview                                                                                                                                 |
|-----|----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| 1   | The process of Ciba Geigy | The catalyst for this process is a divalent copper salt, which is recovered as copper sulfate and refluxed into the reactor. Hydrogen peroxide can be used as an auxiliary catalyst. In the 1990s, three pharmaceutical factories in Germany and Switzerland used this device. Compressed air was used as an oxidant. At 573 K, acetic acid could be decomposed but ammonia could not be decomposed. The oxidation rate reached 95 % to 99 %. This system has been used to treat industrial waste-water and activated sludge. |
| 2   | The process of Bayer Loprox | This process is a low-pressure wet oxidation process developed by Bayer A.G., which is suitable for pretreatment of biochemical processes. Multiple devices have been put into operation. The reactor is a multi-stage bubble column. Organic matter and oxygen are generally reacted under acidic conditions. The reaction temperature and pressure are relatively mild. Usually Fe$^{2+}$ and the intermediate product (H$_2$O$_2$) when forming quinone form a cooperative catalyst. |
| 3   | The process of WPO | This process replaces oxygen (or air) with hydrogen peroxide, eliminating the limitations of the gas-liquid mass transfer process. The combination of hydrogen peroxide and metal salts can significantly improve the TOC removal rate, especially the decomposition rate of low molecular weight carboxylic acids. Under mild conditions (363-406 K, 0.1-0.5 MPa, pH=3), hydrogen peroxide combined with Fe$^{2+}$, with an oxidation rate of 98 %. In 1992, the process was successfully tested in Spain (raw material flow 5 m$^3$/h), and the COD$_{Cr}$ removal rate was higher than 95 %. The Fe-Cu-Mn homogeneous catalyst can oxidize difficult-to-oxidize by-products such as acetic acid, oxalic acid, and succinic acid, and can be recovered after precipitation (pH=9). |
| 4   | The process of Orcan | This process is an improved WPO process, which is mainly used for the pretreatment of refractory waste, and Fe$^{2+}$ and a small amount of hydrogen peroxide (H$_2$O$_2$ mass concentration/COD$_{Cr}$=0.20) are used as catalysts. In 1996, when the first unit was commissioned, the raw material flow was 4 m$^3$/h, and its COD$_{Cr}$ was 710 g/L. |
| 5   | The Catalytic process of IT Enviroscience | This catalytic process (Dow Chemical Company) uses water-soluble auxiliary catalysts, such as bromide and nitrate ion catalysts (1972) and bromine compounds, nitrate ion and manganese ion catalysts (1981). The reaction between catalyst components and organic substances can accelerate the gas-liquid mass transfer process of oxygen; bromine ions can capture the hydrogen element in organic molecules and accelerate their decomposition. |

IT Enviroscience Osaka Gas Co., Ltd. [21] adopted heterogeneous catalytic wet oxidation technology to treat coking waste-water. TiO$_2$ or ZrO$_2$ was used as a catalyst carrier, and one or more active components of Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu, and Au were supported on the catalyst carrier. To avoid clogging, the catalyst was made honeycomb. The results of continuous operation of the
device for 11,000 h showed that the catalyst had no failure phenomenon. Table 3 shows the treatment effect. Its operating conditions are: temperature 250 °C, total pressure 7.0 MPa, air flow 144 m3/h, and liquid-air flow rate 2.5 L/h. According to performance test results, the catalyst can be regenerated once after 5 years of continuous operation for treating waste-water of the same nature as coking waste-water, and the current treatment capacity has been expanded to 60 t/d. And the cost analysis shows that for the treatment of 1t coking waste-water, the operating cost of this process is 2,095 yen, while the operating cost of the traditional process is 3,595 yen, as shown in Table 3.

| Project | pH | NH₃-N (mg/L) | COD₃ (mg/L) | TOD (mg/L) | Phenol (mg/L) | TN (mg/L) | CN (mg/L) | SS (mg/L) | Odor |
|---------|----|-------------|-------------|------------|---------------|----------|---------|-----------|------|
| Raw water | 10.5 | 3080 | 5870 | 17500 | 1700 | 3750 | 15 | 60 | Phenol ammonia |
| Effluent | 6.4 | 3 | 10 | not detected | not detected | 160 | not detected | not detected | No |
| Removal rate (%) | — | 99.9 | 99.9 | 99.8 | 99.9 | 95.7 | 99.9 | 99.9 | — |

Japan Catalytic Chemical Industry Co., Ltd. [22] also achieved success in treating chemical waste-water with heterogeneous catalytic wet oxidation technology. The preparation method of the catalyst is as follows: first, co-precipitation, roasting and other steps are used to prepare Ti-Zr, Ti-Si, and Ti-Zn composite oxide powders; and then, a honeycomb carrier is prepared by adding a binder such as starch. A catalyst is prepared by impregnating a few percent of Mn, Fe, Co, Ni, Ce, W, Cu, Ag, Au, Pt, Pb, Rh, Ru, Ir or other water-insoluble compounds. For waste-water with COD₃ of 40 g/L, total nitrogen of 2.5 g/L, and SS of 10 g/L, under conditions of 240 °C, 50 kg/cm² pressure, and a water flow rate of 11 L/h, COD₃, total nitrogen and ammonia nitrogen removal rates were 99.9 %, 99.2 %, and 99.9 %, respectively.

4. Deactivation of CWAO catalyst

The catalyst must have the characteristics of high activity and good selectivity in application. In addition, it must have high mechanical strength and strong stability, in which the stability affects the ability of the catalyst to decline. After using the catalyst for a period of time, deactivation may occur. The main reasons for deactivation are: outflow of catalyst material and coking. In addition, common inactivation methods are: chemical poisoning caused by poison adsorption, thermal sintering caused by high temperature, charring or deposition inactivation caused by inorganic matter covering the active surface, and chemical sintering caused by the reaction of raw material impurities and active phase.

Catalyst loss is the main cause of deactivation. Its loss is mainly affected by pH. Levec and Pintar [23] found in experiments that the pH of waste-water has an important effect on the oxidation of organics in the liquid phase. Miro et al. [24] used CuO/Al₂O₃ catalyst to treat phenol waste-water at different pH values and found that pH value played a decisive role in catalyst deactivation. Zhang et al. [25] of Canada treated Pd/Al₂O₃ and Pd-Pt/Al₂O₃ with acidic bleaching waste-water and found that under acidic conditions, the reaction efficiency is low and the deactivation rate is high; when the pH value is 7, the loss rate of Pd and Al₂O₃ is small. Next, the Pd-Pt-Ce/Al₂O₃ catalyst was studied, and it was found that when the pH was 7, the catalyst did not lose.

Carbon deposition (also known as catalyst deactivation) is another major cause of catalyst deactivation, which is caused by the deposition of C, N and other substances on the catalyst surface during the reaction. When Belkacermi et al. [26] degraded high-concentration ethanol fermentation waste-water with Mn-Ce and Cu-zeolite catalysts, they found that the degradation rate of waste-water by Mn-Ce catalysts was very high for a certain period of time, and then a downward trend appeared.
The surface of the catalyst was analyzed by photoelectron spectroscopy (ESCA), and carbon deposition was found, which prevented the reactants in the liquid phase from contacting the catalyst surface and deactivated it.

5. Conclusion

For organic waste water that is difficult to biodegrade, the catalytic wet air oxidation (CWAO) technology is used to treat it, and its effect is remarkable. The following 12 kinds of waste-water were treated with CWAO method and achieved good results: papermaking waste-water, dye waste-water, pesticide waste-water, perfume waste-water, phenol waste-water, carbon-containing waste-water, ethanol waste-water, petrochemical company alkali residue waste-water, oil production waste-water, ammonia coking waste-water and pesticide waste-water, emulsified waste-water and desizing waste-water from cleaning workshops. The five processes of Ciba Geigy process, Bayer Loprox process, WPO process, Orcan process and IT Enviroscience catalytic process are typical homogeneous catalytic wet oxidation systems. Due to the low pH value and coking of the reaction system, the heterogeneous catalyst loses its activity. It is necessary to control the reaction conditions to avoid the catalyst losing its activity.

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