

Catalytic wet air oxidation for the treatment of emulsifying wastewater

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Abstract: The wet air oxidation (WAO) and catalytic WAO (CWAO) of the high strength emulsifying wastewater containing nonionic surfactants have been investigated in terms of COD and TOC removal. The WAO and homogeneous CWAO processes were carried out at the temperature from 433 K to 513 K, with initial oxygen pressure 1.2 MPa. It was found that homogeneous catalyst copper($\text{Cu}(\text{NO}_3)_2$) had a fairly good catalytic activity for the WAO process, and the oxidation was catalyzed when the temperature was higher than 473 K. Moreover, several heterogeneous catalysts were proved to be effective for the WAO process. At the temperature 473 K, after 2 h reaction, WAO process could achieve about 75% COD removal and 66% TOC removal, while catalysts $\text{Cu}/\text{Al}_2\text{O}_3$ and $\text{Mn-Ce}/\text{Al}_2\text{O}_3$ elevated the COD removal up to 86%—89% and that of TOC up to 82%. However, complete elimination of COD and TOC was proved to be difficult even the best non-noble catalyst was used. Therefore, the effluent from WAO or CWAO process need to be further disposed. The bioassay proved that the effluent from WAO process was amenable to the biochemical method.

Keywords: catalyst; catalytic wet air oxidation; emulsifying wastewater; wet air oxidation

Introduction

Emulsifying wastewater is a kind of recalcitrant wastewater, which could not be disposed effectively by the conventional methods (Gulyas, 1997) such as flocculation, sedimentation, floatation, extraction and so on. As a result, the treatments of emulsifying wastewater become a severe problem. Polymer surfactants (Mantzavinos, 1997a; 1997b) were often used as bioresistant when its molecular weight was very high; and because there are auxiliary reagents added in emulsifier, which are harmful and toxic to the bacteria, biochemical method can not be used to treat the waste produced during washing oils by the emulsifier. Wet air oxidation (WAO) (Mishra, 1995) and catalytic wet air oxidation (CWAO) process are kinds of elimination technology for the industrial hazardous waste especially for the elimination of high concentration bioresistant organic wastewater. Wet air oxidation (Ellis, 1998) is an aqueous phase oxidation process using molecular oxygen contained in water as an oxidant. The process operates at elevated temperatures and pressures (over 473 K, 4 MPa), organic and other toxic wastes were destroyed and then stabilized during the oxidation process. WAO process was shown to be a feasible method in treating refractory organic pollutants, breaking the recalcitrant organic and then remove its toxicity (Randall, 1980; Mantzavinos, 1997a; 1997b). To provide enough dissolved oxygen for the reaction, a rather high pressure is required in the reactor; it makes the energy consumption very high. The earlier WAO process (Zimmerman Process) needs higher temperature and pressure, which cause its application less practicable than other methods. But CWAO process could be operated under milder conditions with lower temperature and pressure. Catalyst was successfully used in the CWAO process, but it is often made of noble-metals (Maugans, 1997) with very high cost. Therefore, it is expected that noble-metal catalyst could be substituted by non noble-metal one, as that CWAO process could be practiced easily and popularly (Alejandro, 1998).

Based on this, experiments were conducted to examine

the effects of different catalysts such as metal salts, metal oxides, and porous aluminum supported metal or heterogeneous catalyst. All catalysts selected were able to enhance the elimination of the organic in the wastewater, and the activities of different sorts of catalysts were measured by the removal rates of COD and TOC simultaneously. The impact of operating conditions such as temperature on the CWAO process was also tested on the metal salt ($\text{Cu}(\text{NO}_3)_2$) catalyst. Compared with the noble-metal catalysts, the activity of the non-noble metal catalysts was lower than noble ones and it is difficult to achieve complete elimination. Therefore, the effluent from the WAO process need to be further treated for stabilization since it has considerable amounts of organic compounds; the biodegradability of the effluent was also tested.

1 Materials and method

1.1 Materials

The emulsifying wastewater came from a plant producing aluminum plate for automobile air-conditioner. It contained nonionic surfactants, most of them were nonylphenol ethoxylates (NPES) and ethylene/propylene oxide copolymers—materials bio-recalcitrant or partially biodegradable (Kitis, 1999), oil (about 2000 mg/L), NaNO_2 and so on. Its pH was 9.38; its toxicity is equivalent to that of solution HgCl_2 0.12 mg/L. The rest chemicals were analytical reagents.

1.2 Apparatus and procedure

Reaction was carried out in a 2 L stainless autoclave equipped with automatic temperature controller, variable speed stirrer and tachometer. A known amount of wastewater (400 ml, COD 48400 mg/L, TOC 14300 mg/L) and catalyst (if it is necessary) were charged into the autoclave. The reactor was heated by electricity. Under the protection pressure of nitrogen if necessary, the solution started to be stirred by the magnetic agitator at the speed of 500 r/min while the temperature was being elevated up to 10 degree before the fixed one. When the reaction temperature was reached, the first sample was drawn from the autoclave.

Oxygen would be pumped into autoclave directly after wastewater was charged into it.

1.3 Catalyst preparation

Homogeneous salt catalyst used in the CWAO process is $\text{Cu}(\text{NO}_3)_2$ solution, porous alumina supported heterogeneous catalyst was prepared through the method of soaking the porous alumina in the metal salt solution and baked at high temperature.

1.4 Chemical analysis

Sample wastewater drawn was analyzed for COD (by dichromate reflux method), TOC (Shimadzu TOC-500 Analyzer), BOD_5 (5-day BOD Test), volatile organic acid (distilling/acid-base-titration method) and so on.

2 Results and discussion

2.1 Wet air oxidation (WAO) of the emulsifying wastewater

There are factors such as temperature, pressure, inflow concentration etc., which could influence the WAO reaction, among them, the impact of temperature on the efficiency of organic decomposition was the most important one. In the experiment, oxygen was used as the oxidant and it must be supplied enough to avoid the impact of pressure. Besides, the change of pH value and the volatile organic acid of the wastewater during the oxidizing process were also discussed.

2.1.1 Temperature

Temperature plays a decisive role in most of the chemical reactions. Under initial oxygen partial pressure of 1.2 MPa, the impact of temperature on WAO oxidizing reactions from 433 K to 513 K were conducted as shown in Fig.1. At the same inflow concentration, the reaction rate and the removal rate increased considerably with increasing temperature, when the temperature was over 453 K, the reaction rate and removal rate increased more evidently. For example, at 453 K and after 2 h of oxidation, the COD removal was about 64%, but at 473 K, the COD removal was up to 75%. The change of TOC was consistent with that of COD. In WAO process, most of the organic were converted into organic acid firstly, that is to say, the surfactant compounds were turned into intermediates which have low molecular weight (MW), then the intermediates were oxidized under different levels and these made the TOC removal always lower than COD removal. In general, it is easy for the organic to be converted into organic acid but it is difficult that the low MW organic acid was oxidized completely. Therefore, the oxidation of organic acid becomes the rate-control step for the WAO reaction. Elevating reaction temperature could result in more reaction molecules turning into active ones and being oxidized completely, so increasing temperature could lead to the increase of organic removal. At

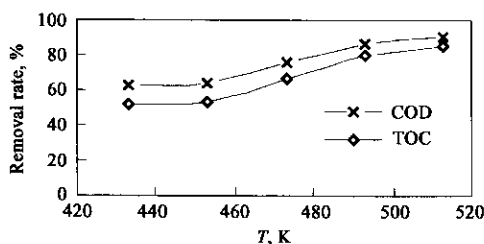


Fig.1 The impact of temperature on the wet air oxidation process

513 K, the organic removal rate was up to 85%—90%.

2.1.2 pH value in the liquid phase

The change of pH value in the liquid phase could reflect the change of the organic in WAO reaction, and the tendency of pH value at different temperatures in the liquid phase was similar to each other (Fig.2).

A sharp decrease occurred on the initial phase, it was the time of the highest production of organic acid while pH declined to the lowest point, then pH value was going up for the oxidization of the organic acid. The higher the pH was, the more complete the compounds were oxidized. But the pH of the effluent after 2 h reaction was lower than 5, which was much lower than that of the inflow. That is to say, the component of the effluent was different from the inflow. The color of effluent was clarified or light yellow at the high removal rate of the organic.

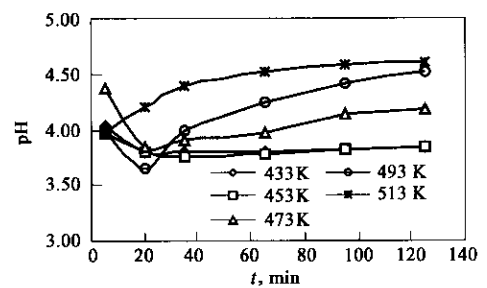


Fig.2 pH curve of the WAO process

2.1.3 The volatile organic acid

The amount of volatile organic acid produced and oxidized was tested at 473 K and after 2 h reaction while testing pH value (Fig.3).

In the initial period, the total volatile organic acid was up to the peak value and then declined, as illustrated in Fig.3 during that time most of the polymer compounds were converted into organic acid and few of them were decomposed completely. The time of the lowest point of pH was 5—10 min later than the appearance of the peak of total volatile organic acid for the complex constitutes of the volatile organic acid. It could not easily ionize like acetic acid and its molecule weight in initial time was too high to ionize. That the surfactant molecular was converted into lower molecular weight compounds decreased the pH value. By comparing Fig.1 with Fig.3, it was found that the contributions of the total volatile organic acid to COD and TOC of the final effluent were respectively 38.4% and 35.7% after 2 h reaction at 473 K. The GC results also shown that the final effluent included not only volatile organic acid as acetic acid but also lower molecular alcohol such as methanol, ethanol, lower ether and lower ester and so on; the total organic acid

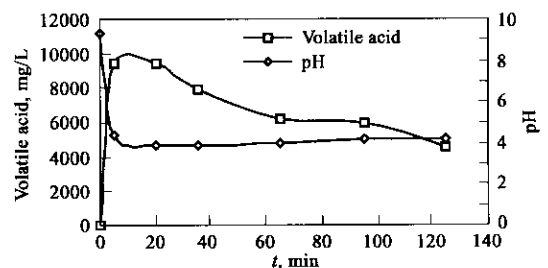


Fig.3 The curve of the volatile acid of WAO at 473 K

in effluent may be up to 50% (Tang, 2001).

2.2 Homogeneous catalytic oxidation of the emulsifying wastewater

In general heterogeneous catalysts are applied in industrial production. In this study, catalyst with the selected elements was used to obtain high removal efficiency at lower temperature.

At present inflow concentration of the experiment, it was reported that adding 200 mg/L metal ion or so could achieve a good catalytic activity. The catalytic activity of the copper ion for the WAO process was investigated at temperature ranging from 433 K to 513 K. Fig. 4 shows that the comparison of the organic removal rate between the catalyzed and the non-catalyzed at the condition of different temperatures, with oxygen partial pressure 1.2 MPa, after 2 h of reaction.

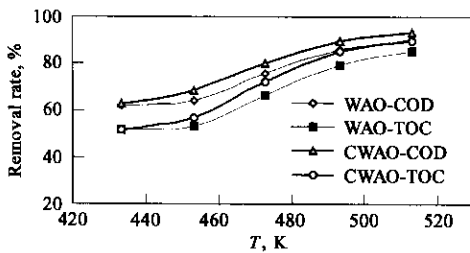


Fig. 4 Comparison between uncatalysed WAO and homogenous catalysed WAO of the wastewater

The result indicates catalytic activity of copper ion changed higher with increasing temperature. In the case of TOC removal, catalyst played a more important role on the oxidation. At the temperature above 473 K, the rate of TOC removal was elevated rapidly by adding homogeneous catalysts. It means that catalyst not only enhanced the initial rates of reaction, but also considerably increased the decomposing rates of the organic acids and other kinds of intermediates. Compared with the removal rate at the temperature 453 K while COD removal rate was elevated about 3.4% and that of TOC was elevated 3.6%, the rate of COD removal at 473 K was elevated 5% and that of TOC increased 6.5%.

2.3 Heterogeneous catalytic WAO of the emulsifying wastewater

Based on the above results, heterogeneous catalytic WAO experiment was carried out at the temperature of 473 K (oxygen partial pressure 1.2 MPa) for the purpose of achieving better organic removal rate than that of WAO process at higher temperature. A same initial oxygen partial pressure was kept for comparison.

The heterogeneous catalyst was powder metal oxide, such as CuO, MnO₂, Co₂O₃ etc, among them CuO and MnO₂ have very good catalytic activity, but Co₂O₃ has no activity for the CWAO process. Table 1 shows the results of heterogeneous CWAO process at the temperature 473 K, with initial oxygen partial pressure 1.2 MPa, after 2 h reaction while adding 200 mg/L active metal of catalysts. CuO has the best activity for CWAO. The result in the case of COD was consistent with that of TOC.

When active alumina was used as the catalyst supportor, there were 3 kinds of heterogeneous catalysts were prepared. The amount of the catalyst was 2.5 g. Fig. 5 and Fig. 6 show among Cu/Al₂O₃ catalyst, complex Cu-Ce/Al₂O₃ catalyst and

Mn-Ce/Al₂O₃, catalyst Cu/Al₂O₃ had the best activity at 2 h reaction. The 2 h removal rate of COD was as high as 89%, and that of TOC nearly reach 82%. As for COD removal rate, catalyst Mn-Ce/Al₂O₃ also had good activity but lower than that of catalyst Cu/Al₂O₃. On the other hand, Mn-Ce/Al₂O₃ had the same activity as that of Cu/Al₂O₃ as for TOC removal rate after 2 h reaction. It is likely that the two catalysts had different reaction path for catalytic reaction. In brief, more intermediates were produced during the CWAO by the use of catalyst Cu/Al₂O₃ than that of Mn-Ce/Al₂O₃. Catalyst Mn-Ce/Al₂O₃ had the best activity for both COD and TOC removal, that is to say, catalyst Mn-Ce/Al₂O₃ had a better selectivity for the complete oxidation path. In addition, it was reported (Qin, 1998) that catalyst harbored Mn-Ce complex oxide had good activity for oxidizing nitrogen compounds, but the wastewater used in this experiment had little organic nitrogen compound with a lot of chain-molecular organic surfactants. It means that the catalyst Mn-Ce/Al₂O₃ also had better activity for the complete oxidation of chain-molecular organics than that of catalyst Cu/Al₂O₃.

Table 1 Catalytic activity of the oxide powder catalyst

Catalyst	COD removal, %	TOC removal, %
CuO	79.53	70.52
MnO ₂	77.34	68.50
Co ₂ O ₃	73.78	65.59
Blank	75.44	66.36

Notes: $T = 473$ K, $P_{O_2} = 1.2$ MPa, 2 h reaction

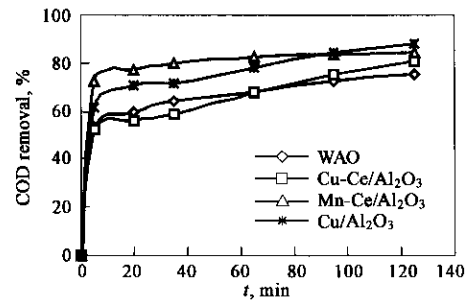


Fig. 5 Activity of heterogeneous catalysts

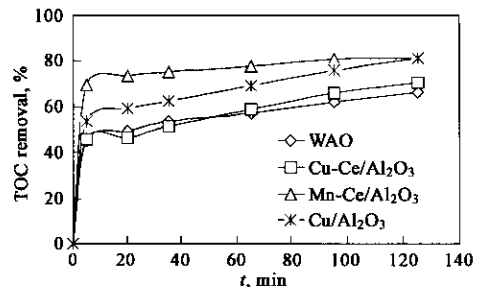


Fig. 6 Activity of heterogeneous catalysts

2.4 Bioassay of the effluent from WAO

A considerate organic removal rate was achieved in the treatment of the emulsifying wastewater by WAO and CWAO process, but even if the best catalyst was used, a higher removal rate above or more than 90% could not be achieved under this similar condition, the effluent from WAO or CWAO process still had heavy concentration of the organic.

The constituents of the effluent were much different from the inflow wastewater. Virtually the effluent would be biodegradable if the organic removal rate was rather good since WAO process has good ability of detoxification. The bioassay of the effluent from WAO process was made through testing its BOD₅/COD and SBR (sequential batch reactor) process, at 473 K with COD removal 75%, the effluent of 2 hours reaction, its BOD₅/COD was 0.51. The result from SBR experiment also proved its biodegradability. If the organic removal rate were higher than this, the coefficient of BOD₅/COD would be higher. Take it into consideration that wet oxidation process needs fairly high capital and operational cost; it would be a practicable strategy to utilize WAO or CWAO process as a pretreatment technology, and to use bio-chemical method as the successor disposal process.

3 Conclusions

Wet air oxidation and catalytic WAO process were feasible methods to treat the emulsifying wastewater, which harbored nonionic surfactants. Organic waste removal rate would be promoted by the use of heterogeneous catalysts such as Cu/Al₂O₃ and Mn-Ce/Al₂O₃ at 473 K, it could reach the organic elimination equal to that of under the condition of 493–513 K with the same initial oxygen supply. The reaction of WAO and CWAO were first order magnitude for the organic concentration. Complete removal of the waste could not be achieved even though the best non-noble metal catalyst was used; a successor waste elimination method should be taken into account. Bio-chemical technology could be used in the successor treatment process for the effluent

from the WAO process was biodegradable. In the end, it should be pointed out that the metal leaching of the catalyst and the impact of the leaching on the effectiveness of the bio-chemical process should be studied in detail.

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