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Homogeneous catalytic wet air oxidation for the treatment of textile wastewaters

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Abstract: An extensive series of experiments was carried out in order to identify suitable catalysts to boost the reaction rate of wet air oxidation of real textile wastewaters at relatively mild temperature and pressure. Experimental results indicated that all catalysts tested in this investigation had shown an impressive increase in the initial COD and TOC removal rate as well as the COD and TOC removal levels in two hours reaction. Among all the catalysts tested, copper salts were more effective than the rest. Anions of the salt solutions also played a role in the catalytic process with nitrate ions having better effect than sulfate ions. Hence copper nitrates were more effective than copper sulfates. It was also found that a mixture of salts with different metals performed better than either of the component single salt alone.

Key words: wet air oxidation; catalysis; textile wastewater

Introduction

The textile wastewaters are one of the major pollution concerns in China water environment. These wastewaters are mainly effluents from the desizing, printing and dyeing processes. The pollutants in desizing wastewaters depend widely on the fibre desized. The nature fibre desizing wastewater is characterized by its high chemical oxygen demand (COD) typically in the range of 10000 to 40000 mg/L as well as heavy BOD of 5000 to 10000 mg/L. The high ratio of BOD to COD implies this type of desizing wastewater is biodegradable. Whereas the man-made fibre desizing wastewater is also of high COD but biological refractory due to its high contents of polyvinyl alcohol. Printing and dyeing wastewaters are, however, not only of high COD and low BOD but also of heavy colour.

Treatment of textile wastewaters by biological degradation is not only unsuitable for refractory printing and dyeing wastewater but also for less biodegradable man made fibre desizing wastewater. Membrane technique has been proved to be a feasible method to concentrate textile wastewater, but the concentrate should be treated before discharge although the permeate can be reused (Ben, 1993). Wet air oxidation (WAO), which mineralizes pollutants at elevated temperature and pressure, has the ability to convert most organic and inorganic compounds into carbon dioxide, water and mineral acids, with no additional sludge or concentrated wastes being produced during the treatment process. It has been proved to be an efficient method of COD removal from textile wastewaters (Lei, 1996). The high temperature and high pressure employed, however, are not attractive to the leaching and dyeing industries. In order to considerably relax the reaction conditions, a small amount of catalysts can be used. Thus the process becomes catalytic wet air oxidation (CWAO).

Most of the investigations on CWAO is focused on pure compounds destruction, only a few are published on catalytic oxidation of the real wastewater (Mantzavinos, 1996; Ajit, 1974; Pintar, 1992; Leavitt, 1990). Because catalyst is selective and can be easily poisoned during real wastewater treatment, catalyst having high activity in the treatment of pure compounds may show different effect in the real wastewater treatment. Therefore, it is very important to treat real wastewater with CWAO in order for the results to be useful in wastewater treatment practice. Thus, it becomes the objective of the present study.

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1 Experimental

The real desizing, printing and dyeing wastewaters used in this study were collected from a textile company. The oxidation of the wastewater was carried out in a two-liter autoclave equipped with a cooling coil and magnetic stirring system. A schematic diagram of the catalytic wet air oxidation system is shown in Fig. 1.

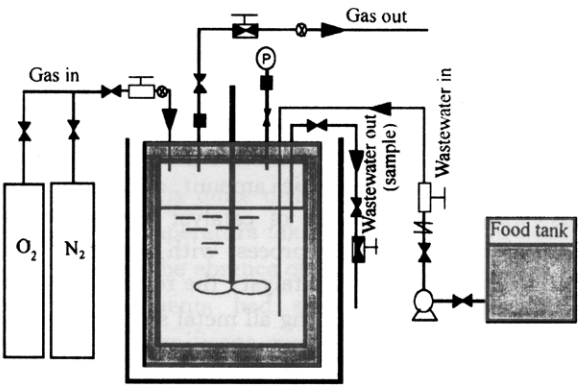

Fig. 1 Schematic of the catalytic wet air oxidation system

The catalysts used in this study can be basically classified into two major groups: nitrates and sulfates of transitive metals. The selection of metal is based on the fact that heavy metal ions, particularly those that possess two or more valency states between which there is a suitable oxidation-reduction potential so that they can react with peroxides to produce free hydroxyl radicals. Other requirements for transitive metals are: easily obtainable, cheap and less toxic. Hence iron, copper and manganese were chosen.

Tested catalysts include $CuSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $MnSO_4$, $Cu(NO_3)_2$, $Fe(NO_3)_3$ and $Mn(NO_3)_2$. The copper sulfate, ferrous sulfate-7-hydrate, manganese sulfate-4-hydrate and iron sulfate are from Riedel-de haën. The copper nitrate-3-hydrate is from Nacalci Tesque Inc. The manganese nitrate-4-hydrate and iron nitrate-9-hydrate are also from Riedel-de haën. In addition, $FeCl_2$, ferrous chloride-4-hydrate(Sigma Chemical Co.) was also tested.

The operating procedures of wastewater treatment are as follows: first the reaction was preheated to 60—70℃. Then 1.4 liters(70% of the capacity of the reactor) of wastewater, together with the catalyst if required, were charged into the reactor. Pure nitrogen was used to purge the air inside the reactor at a total pressure of 1 MPa for two minutes, after which the system was isolated. The reactor was heated to the desired reaction temperature which tool approximately one to two hours. Once the selected reaction temperature was reached, pure oxygen was introduced into the reactor and the reaction was assumed to start(reaction time $t = 0$). At designated time intervals thereafter, liquid samples were taken from the reactor. At the end of the reaction time, the heating jacket was turned off and the reactor was cooled for half an hour. Cooling water was then passed through the cooling coil to further cool the reactor to 60—70℃. Pure nitrogen was passed through the reactor to sweep the treated wastewater and the spent catalyst. Between experiments, the reactor was cleaned by filling it with deionized water and running the stirrer at 1000 r/min for 5 minutes. This cleaning step was repeated three or four times until the discharged water was visibly clean.

Liquid samples taken during the reaction were allowed to cool down to ambient temperature. Any sediment present was allowed to settle down. Then the supernatant liquid was analyzed for BOD, COD and TOC contents. The COD values were determined by a HACH DR/2000(USA) direct reading spectrophotometer using a HACH COD reactor. The TOC results were determined by a Shimadzu TOC-5000 analyzer. The method for quantification of BOD_5 was adopted from the standard using traditional 5 days culture. The biodegradability is defined as the ratio of BOD_5 to COD. The TOC or COD removal is calculated according to Equation(1) or (2), respectively.

$$\eta_{TOC}(\%) = \frac{TOC_{in} - TOC_t}{TOC_{in}} \times 100\%, \quad (1)$$

$$\eta_{COD}(\%) = \frac{COD_{in} - COD_t}{COD_{in}} \times 100\%, \quad (2)$$

where, TOC_t(COD_t) is defined as the TOC(COD) value at reaction time t; TOC_{in}(COD_{in}) is

the initial TOC (COD) value of fresh wastewater.

2 Results and discussion

The catalytic wet air oxidation of textile wastewaters from nature fibre desizing process was studied first using sulfate catalysts. This was conducted at a fixed temperature of 240℃. The oxygen partial pressure was kept at 1.5 MPa(at a reference temperature of 25℃) which is twice the required stoichiometric amount of chemical oxygen demand of the nature fibre desizing wastewater. The amount of catalyst added was 100 mg metal ions per liter wastewater. The progress of the oxidation process with various sulfate catalysts is shown in Fig. 2. Compared with the results without any catalyst, the removal rates for COD and TOC are obviously enhanced by all the tested catalysts. Among all metal sulfate catalysts employed except Mn^{2+}, the relative catalytic activity is found the increase according to the following sequence as: $Fe^{3+} < Cu^{2+} < Fe^{2+}$. The catalytic activity for Mn^{2+} is seen comparable with Fe^{2+} initially but gradually deviates from Fe^{2+}. After 150 minutes reaction, Mn^{2+} becomes the worst among the four tested. Shown in Fig. 3 is the effects on the treatment of nature fibre desizing wastewater in the presence of metal nitrates catalysts. The operating conditions are the same as those of Fig. 2. It can be seen that the metal nitrate catalysts posses a higher catalytic activity than sulfates. The behavior of Mn^{2+} is similar to that in Fig. 2. The rest metal activity follows the sequence as : $Fe^{2+} < Fe^{3+} < Cu^{2+}$. It is interesting to note that the sequences for sulfate and nitrate catalysts are not the same. This implies that different anions can also affect the catalytic activity. For example, copper nitrate performs better than copper sulfate. Table 1 presents the comparison of different salt catalysts at reaction time of 30 minutes.

Table 1 Comparison of various catalysts on COD, TOC removal at 30 min reaction time

	$CuSO_4$	$FeSO_4$	$MnSO_4$	$Fe_2(SO_4)_3$	None
COD removal, %	68	79	74	61	31
TOC removal, %	62	72	67	54	26
	$Cu(NO_3)_2$	$FeCl_2$	$Mn(NO_3)_2$	$Fe(NO_3)_3$	None
COD removal, %	77	69	75	69	31
TOC removal, %	77	59	71	64	26

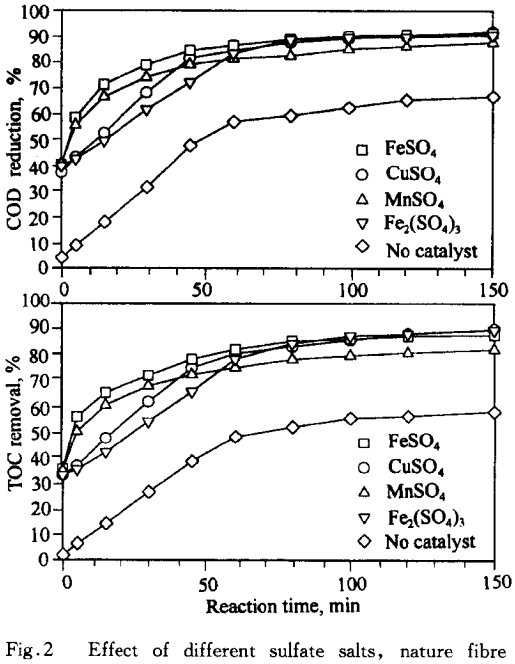

Fig.2 Effect of different sulfate salts, nature fibre desizing wastewater

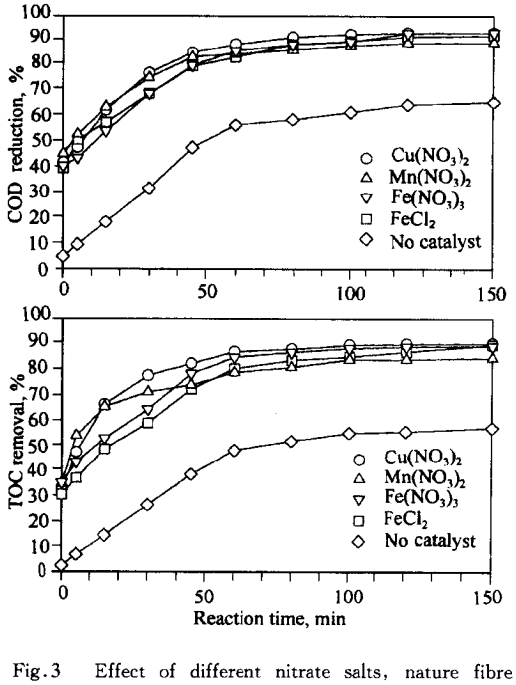

Fig.3 Effect of different nitrate salts, nature fibre desizing wastewater

Amongst all transition metals employed in this study, $Cu(NO_3)_2$ present the best catalytic activity. It is speculated that the reason for such a behavior may be because of the d^9 electric layer structure of cupric ion. So it can easily form octahedral complex with NO_3^- or organic molecule. After organic are oxidized, the cupric ion can be released. Therefore, copper nitrate is a better catalyst compared with ferrous sulfate in the treating nature fibre desizing wastewater.

It is found that the initial value for CWAO at $t = 0$ is quite different from that of WAO process. Since heating the reactor to the desired reaction temperature takes from one to two hours. The COD and TOC variations during the heating period in the absence of oxygen have occurred by thermal decomposition. However, our previous experiments had shown that the thermal decomposition of nature fibre desizing wastewater was insignificant even though by keeping the reactor at 290℃ for up to 150 minutes in the absence of oxygen and catalyst(Lei, 1996). When adding catalyst, it is interesting to note that the initial removal during the heating period (at $t = 0$) has been significantly improved compared with that without catalyst. Because metal salts can form the complex compounds in the presence of high pH value, these formed complex may play an important role in the thermal coagulation at elevated temperature. Preliminary runs using the same concentrations of these metal salts showed that the coagulation effects on removal rates was insignificant at the ambient temperature. Thus reflects that the high molecular weight pollutants are first decomposed by means of thermal destruction, then form intermediates that can be relatively easy to coagulate with the complex compounds formed through added metal salts.

In addition, some results showed that ferrous sulfate has demonstrated a higher catalytic activity compared with the rest sulfates. The question remained is how these two effective salts, copper nitrate and ferrous sulfate would affect WAO when both of them are present. Fig. 4 shows the removal rates for COD and TOC at various doses of ferrous and cupric ions. The total amount of catalyst added remained at 100 mg/L calculated based on metal ion concentrations. As the share of cupric ion increased, the COD and TOC removal rates are evidently improved, reflecting that cupric ion plays a major role in the catalytic oxidation. Compared with the effects of catalyzing by

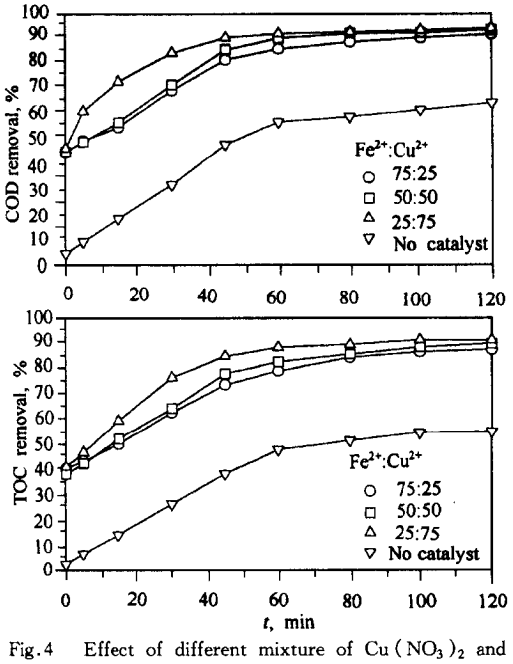

Fig.4 Effect of different mixture of $Cu(NO_3)_2$ and $FeSO_4$, nature fibre desizing wastewater

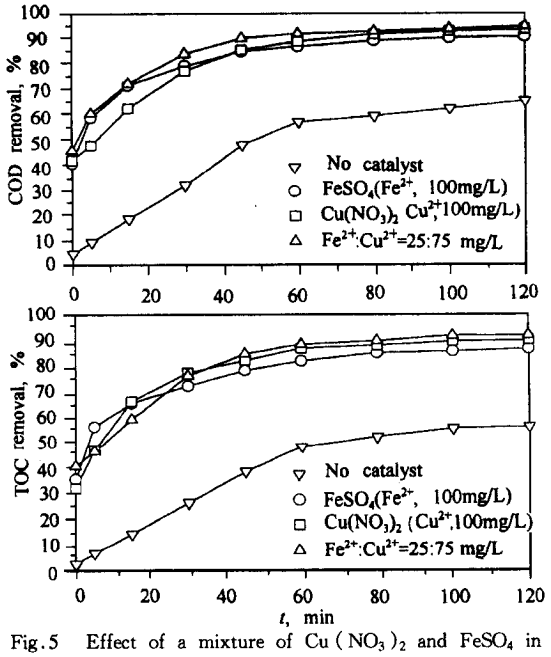

Fig.5 Effect of a mixture of $Cu(NO_3)_2$ and $FeSO_4$ in comparison with pure $Cu(NO_3)_2$ and $FeSO_4$ mix salts with single salt

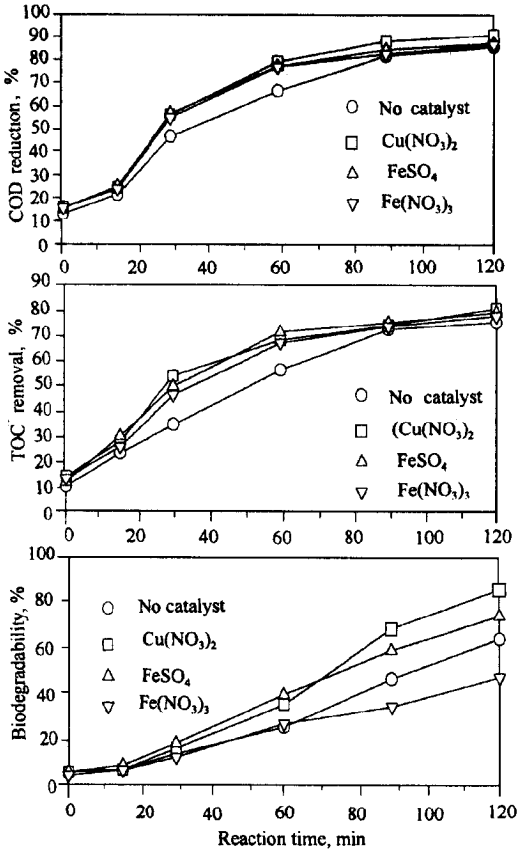

Fig.6 Effect of different catalysts, PVA containing desizing wastewater

single metal salt catalyst, as shown in Fig. 5, the salt mixture demonstrates a better catalytic activity. With CWAO for treating nature fibre desizing wastewater conducted at 240℃ and 1.5 MPa oxygen partial pressure, 90% COD removal can be achieved within 90 minutes reaction time in the presence of 75 mg/L cupric ion and 25 mg/L ferrous ion.

Copper nitrate and ferrous sulfate have been proved to be effective catalysts in the treatment of nature fibre desizing wastewater. The same attempt has been made to employ them in the treatment of PVA containing man-made fibre desizing wastewater. Catalysts in the form of metal salt solution are added to the reactor to promote the oxidation processes. Three catalysts of transition metal salt solutions, $Cu(NO_3)_2$, $FeSO_4$, and $Fe(NO_3)_3$, were tested. The amount of catalysts in terms of metal ion concentration was 100 mg/L. The reaction conditions were kept at a temperature of 240℃ and an oxygen partial pressure of 1.66 MPa at the reference of 25℃ in all cases. The wastewater treatment results are shown in Fig. 6 as COD and TOC removals versus reaction time. With a catalyst added, the wastewater treatment is improved slightly. In addition, the catalytic effect can not be distinguished among three catalysts tested. It is notable that Cu^{2+} can remarkably improve the biodegradability for the PVA containing desizing wastewater. After 120 minutes reaction, the biodegradability can be enhanced from the initial value of 0.1 to a high value of 0.8, while that of WAO is slightly higher than 0.6. The Fe^{3+} catalyst, however, shows a decrease in biodegradability compared to that without catalyst.

The effect of catalyst concentration on treatment of PVA containing wastewater was then investigated using $FeSO_4$. It is obvious that higher removal rates can be achieved with Fe^{2+} concentration increased as shown in Fig. 7. Theoretically, the reaction rate should not depend on the concentration of catalyst once there is a different supply. The experimental results shown in Fig. 7 are very interesting. When the catalyst concentration increases from 50 mg/L to 100 mg/l, there is no significant improvement in TOC removal. Further increase of Fe^{2+} concentration to 400 mg/L shows a distinct difference of both COD and TOC removals. When the ferrous ion concentration is 800 mg/L, only a slight improvement in COD and TOC removals was observed comparing with that of 400 mg/L. Thus it indicates that the Fe^{2+} concentration of 400 mg/L may be sufficient in catalyzing wet air oxidation reaction for the treatment of PVA containing desizing wastewater.

Four catalysts of transition metal solution, $Cu(NO_3)_2$, $Mn(NO)_2$, $FeSO_4$ and $CuSO_4$, were tested in CWAO of another biological refractory wastewater, printing and dyeing wastewater. The amount of catalysts in terms of metal ion concentration used in the reaction was 2000 mg/L. The reaction conditions were kept at a temperature of 200℃ and an oxygen partial pressure of 2.65 MPa in all cases. The wastewater treatment results are shown in Fig. 8 as COD and TOC removals

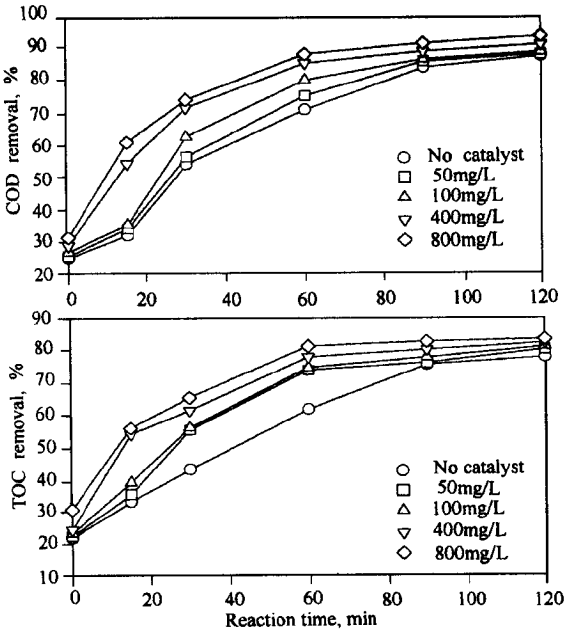

Fig. 7 Effect of $FeSO_4$ concentration, PVA containing desizing wastewater

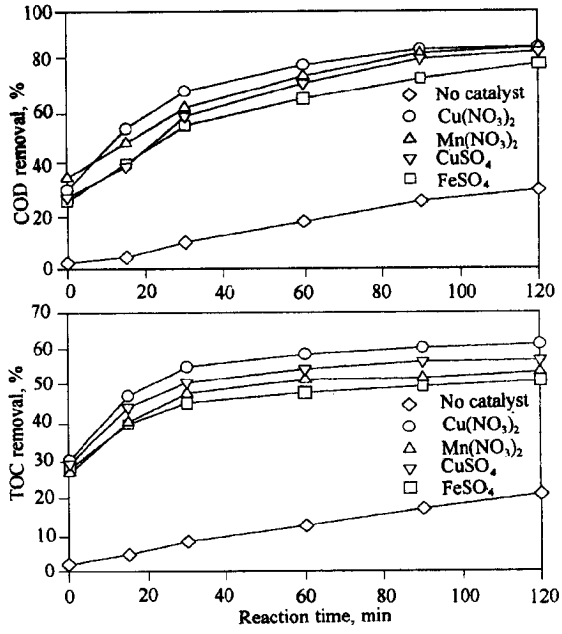

Fig. 8 Effect of different catalysts, printing and dyeing wastewater

versus reaction time. With a catalyst added, the COD and TOC removal rates are significantly improved. The COD and TOC removals are approximately three times higher than those without catalyst after two hours reaction. Copper nitrate is the most efficient one among the four catalysts used, similar to that for nature fibre desizing wastewater treatment.

3 Conclusion

Transition metal salts used in this investigation have been proved to be effective catalysts to boost the reaction rate of wet air oxidation of real textile wastewaters at relatively mild temperature and pressure. Experimental results indicate that all catalysts tested have shown an impressive increase in the initial COD and TOC removal rate as well as the COD and TOC removal levels in two hours reaction. Among all the catalysts tested, copper salts are more effective than the rest. Nitrate ions have better effect than sulfate ions which indicates nitrate anions also play a role in the catalysis process. It has been found that a mixture of copper and ferrous metals performs slightly better than either of the component single salt. The results have indicated that the mixture of Cu^{2+} and Fe^{2+} ions possesses the best catalytic activity in the treatment of nature fibre desizing wastewater. No significant difference was observed among the ions in affecting the TOC and COD removals for the treatment of PVA containing desizing wastewater. The COD and TOC removals for treating this type of wastewater did show an increase with the Fe^{2+} concentration until about 400 mg/L. Amongst all tested catalysts in the treatment of printing and dyeing wastewater copper nitrate is the best one.

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