

## Pretreatment of apramycin wastewater by catalytic wet air oxidation

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**Abstract:** The pretreatment technology of wet air oxidation (WAO) and coagulation and acidic hydrolysis for apramycin wastewater was investigated in this paper. The COD, apramycin,  $\text{NH}_4^+$  concentration, and the ratio of  $\text{BOD}_5/\text{COD}$  were analyzed, and the color and odor of the effluent were observed. WAO of apramycin wastewater, without catalyst and with  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts, was carried out at degradation temperature of 200 °C and the total pressure of 4 MPa in a 1 L batch reactor. The result showed that the apramycin removals were respectively 50.2% and 55.0%, COD removals were 40.0% and 46.0%, and the ratio of  $\text{BOD}_5/\text{COD}$  was increased to 0.49 and 0.54 with  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts in catalytic wet air oxidation (CWAO) after the reaction of 150 min. With the pretreatment of coagulation and acidic hydrolysis, COD and apramycin removals were slight decreased, and the ratio of  $\text{BOD}_5/\text{COD}$  was increased to 0.45, and the effluents was not suitable to biological treatment. The color and odor of the wastewater were effectively controlled and the reaction time was obviously shortened with WAO.  $\text{HO}_2\cdot$  may promote organic compounds oxidized in WAO of the apramycin wastewater. The addition of  $\text{CeO}_2$  could promote the activity and stability of  $\text{RuO}_2/\text{Al}_2\text{O}_3$  in WAO of apramycin wastewater.

**Keywords:** catalytic wet air oxidation (CWAO); metal catalyst; antibiotic production wastewater; apramycin wastewater

### Introduction

Pharmaceutical industry becomes more and more important all over the world. In China, there are more than 300 plants manufacturing antibiotic production. However, the plants often produce a lot of wastewater containing high concentrated, color toxic organic compounds. If the pollutants are discharged without treatment, severe problem would be caused to the environment and to human being and animal. The discharge laws for the wastewater have been established by governments. Therefore, the effective treatment technologies have received more attention to decrease the chemical oxygen demand (COD) and toxic organic compounds in the wastewater, such as: physical treatment (adsorption, etc.), chemical treatment (wet air oxidation (WAO), photocatalysis oxidation, ozonation, UV irradiation, etc.), biological treatment and incineration, etc. (Luck, 1999; Kommuller, 2003; Lim, 2003; Qu, 2004; Niu, 2004). Physical-chemical, hydrolytic acidification, aerobic and anaerobic biological treatments are often used to treat the wastewater, but these technologies have some disadvantages (Alaton, 2004). In China, the pretreatment method of coagulation and acidic hydrolysis is often applied to treat the antibiotic production wastewater because of the simple process.

WAO has been proved to be an effective treatment technology for the wastewater containing high concentrated and toxic contaminants, which are too dilute to be incineration and are unfeasible for the biological treatment because of the toxicity to bacteria. In the WAO process, organic compounds are oxidized into carbon dioxide, water and other innocuous end products under high temperature (125–320 °C) and high pressure (0.5–20 MPa) using oxygen or air as oxidant gas (Mishra, 1995). In the last 20 years, catalytic wet air oxidation (CWAO) has been developed in order to operate under mild conditions, shorten reaction time, and promote the refractory compound oxidized.

Homogenous catalysts, for example Cu and Fe salts, have good activity in CWAO of organic compounds, but additional steps to remove and recover metal ions are necessary (Miró, 1999; Verenich, 2000; Kayan, 2004). Heterogeneous catalysts are more promising for treating the wastewater. Now the development of active and stable heterogeneous catalysts have gained great attention. Noble metal catalysts (Pt, Pd, Ru, Ir) in CWAO have been emphasized by previous study, which show an excellent activity and stability (Oliviero, 2000; Trawczynski, 2003; Cybulski, 2004).

CWAO has been applied in treating different pollutants, and CWAO of the industrial wastewater is also studied. Besson *et al.* studied CWAO of acidic and alkaline Kraft bleach plant effluents over  $\text{Ru}/\text{TiO}_2$  and  $\text{Ru}/\text{ZrO}_2$  catalysts at 463 K and 5.5 MPa total air pressure in a batch slurry reactor (Pintar, 2001). Experiment results showed that TOC removals were respectively up to 88% and 79%, and no leaching of Ru, Ti or Zr was detected. Zhang *et al.* investigated CWAO of paper and pulp mills wastewater in Kraft bleach plant with Pt-Pd-Ce/alumina, Pt-Pd/alumina and Pd/alumina catalyst catalysts at 423–463 K and 1.5 MPa total pressure in a slurry reactor (Zhang, 1998; 1999). Pt-Pd-Ce/alumina catalyst showed the better activity and stability than other catalysts. 65% TOC and 99% color were removed at 443 K after 3 h reaction over Pt-Pd-Ce/alumina. CWAO of a typical high concentrated industrial wastewater of Afyon alcaolide factory was also studied (Kacar, 2004). The results showed that the  $\text{BOD}_5/\text{COD}$  ratio was increased from 0.15 to above 0.5 by using  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  salt catalysts after 2 h oxidation. In Zhu's study, copper (Cu), cerium (Ce), cadmium (Cd) and cobalt-bismuthide (Co-Bi) catalysts were used to treat H-acid manufacturing process wastewater at 473 K, oxygen partial pressure of 3 MPa and pH value of 12. H-acid was totally decomposed in 5 min, and the COD removal rate was over 90% in 30 min (Zhu, 2002). These studies indicate that CWAO is a great potential and attentive pretreatment

technology for multi-component industrial wastewater.

However, the study of WAO of pharmaceutical wastewater is very limited. The purpose of the paper is to investigate the pretreatment of the antibiotic production wastewater, apramycin wastewater, with both WAO and coagulation and hydrolytic acidification methods. The wastewater came from Puyang Pharmaceutical Plant in Henan Province of China. COD concentration of the wastewater was about 5000 mg/L, and toxic compound, apramycin, was about 130 mg/L. The structure was shown in Fig. 1. The wastewater was brown color and strongly odor. The removal of apramycin, COD,  $\text{NH}_3\text{-N}$ , and the change of the color, odor and the reaction time were compared with two kinds of pretreatment methods. Moreover, the ratio of biological oxygen demand to chemical oxygen demand ( $\text{BOD}_5/\text{COD}$ ) was studied in order to evaluate the biodegradability of apramycin wastewater using two pretreatment methods. On the other hand,  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts were prepared and used to treat apramycin wastewater in WAO. The catalysts activity and stability was investigated in a batch reactor.

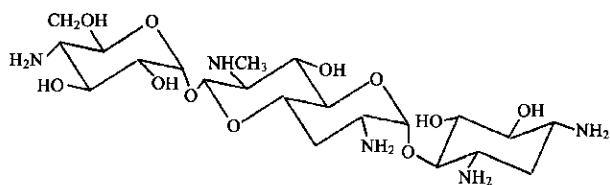


Fig. 1 The chemical structure of apramycin

## 1 Materials and methods

### 1.1 Experimental procedures

WAO of apramycin wastewater was carried out in a 1 L reactor equipped with a magnetically driven stirrer ensuring good mass transfer from the gas to the liquid phase and to the catalyst. First, 500 ml apramycin wastewater and 1 g of catalysts were charged into the reactor. The reaction was performed at the temperature of 200 °C and the total pressure of 4 MPa in 150 min. The flow diagram of the experimental setup is showed in Fig. 2. The process was as that in the previous study (Zhu, 2002).

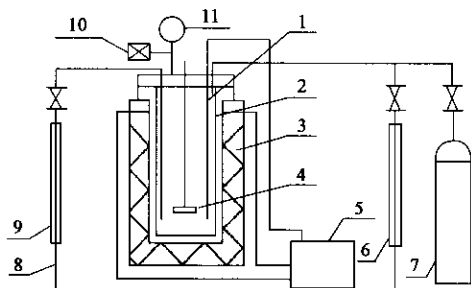


Fig. 2 Schematic view of reactor

1. thermocouple; 2. reactor body; 3. heating jacket; 4. magnetic stirrer; 5. controller; 6. gas sampling valve; 7. oxygen cylinder; 8. liquid sampling valve; 9. cooling jacket; 10. relief valve; 11. pressure gauge

In the pharmaceutical plant of Henan Province, the flow chart of treating apramycin wastewater with biological treatment is shown in Fig. 3. The wastewater was treated with

coagulation method where  $\text{FeSO}_4$  was selected as coagulants, then the effluent entered into the acidic hydrolysis reactor. In the process of acidic hydrolysis, complex organic compounds were degraded to low molecular weight compounds. The sludge was firstly acclimated for 60 d, then the apramycin wastewater entered into the acidic hydrolysis reactor, and run for 10 d. The effluent was analyzed. Finally, the wastewater flowed into the anaerobic reactor, and then into aerobic reactor. COD of the effluent was measured.

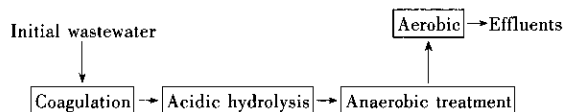


Fig. 3 The flow chart of biological treatment method for apramycin wastewater in the plant

### 1.2 Catalyst preparation

$\gamma\text{-Al}_2\text{O}_3$  (BET: 153  $\text{m}^2/\text{g}$ , 1—2 mm diameter) was used as a support of the catalysts.  $\text{RuO}_2/\text{Al}_2\text{O}_3$  catalyst was prepared by impregnation of  $\gamma\text{-Al}_2\text{O}_3$  with aqueous solution of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ . The preparation process of  $\text{RuO}_2/\text{Al}_2\text{O}_3$  catalyst was described in our study (Yang, 2004).  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalyst was prepared by consecutive impregnation procedure. Ce as a promoter was firstly added on  $\gamma\text{-Al}_2\text{O}_3$ . The support was dipped into the  $\text{Ce}(\text{NO}_3)_3$ , dried at 110 °C overnight, and calcined at 400 °C for 3 h in air, then followed for impregnation of Ru as that of  $\text{RuO}_2/\text{Al}_2\text{O}_3$  catalyst to prepare  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalyst.

### 1.3 Analysis methods

The concentration of the effluents of COD,  $\text{BOD}_5$ , and  $\text{NH}_3\text{-N}$  was determined with the standard methods for water and wastewater examination. The apramycin concentration of wastewater was measured by UV spectrometer of 752. Leaching of the catalysts in the liquid was analyzed with Plasma1000 ICP.

## 2 Results and discussion

### 2.1 Apramycin and $\text{NH}_3\text{-N}$ removal

Fig. 4 shows the apramycin concentration of wastewater after the pretreatments of WAO and coagulation and acidic hydrolysis. The toxic pollutant, apramycin, decreased with two kinds pretreatments methods. 45% apramycin was decreased with no-catalyst in WAO of the wastewater, moreover, 50.2% and 55.1% apramycin were removed with  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts in WAO at the reaction temperature of 200 °C and the total pressure of 4 MPa after 150 min run. But apramycin removal was only 40% after 10 d run with coagulation and acidic hydrolysis. This indicated that CWAO of the toxic wastewater was more effective, and the reaction time that WAO oxidized apramycin was obviously shortened.  $\text{NH}_3\text{-N}$  concentration was measured in the effluents, and the results are showed in Fig. 4. It was found that the concentration of  $\text{NH}_3\text{-N}$  increased in WAO, while it decreased in coagulation and acidic hydrolysis method. In WAO process the high molecular weight compounds containing N element, for example apramycin, was oxidized to low molecular weight compounds, it might result in that a part of N element of organic compounds was transformed to nitrite or nitrate ions, so  $\text{NH}_3\text{-N}$  concentration

increased in WAO. This meant that the toxic compounds and the toxicity of the effluents were decreased, it was helpful that the effluent could be easily treated with biological technology. In the process of coagulation and acidic hydrolysis, the bacteria took N element as a kind of nutrient compounds, but apramycin had toxic role to the bacteria, so the reaction time was very long, and  $\text{NH}_3\text{-N}$  concentration slightly decreased in the process.

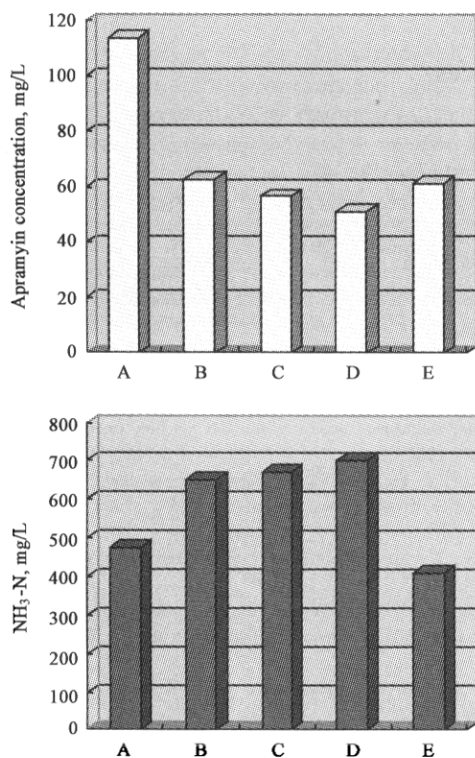


Fig.4 The Apramycin and  $\text{NH}_3\text{-N}$  concentration of the effluent with the different pretreatment methods

A. the initial wastewater; B. WAO; C.  $\text{RuO}_2\text{-Al}_2\text{O}_3$ ; D.  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$ ; E. coagulation and acidic hydrolysis

## 2.2 COD removal and the biodegradability

Fig.5 shows the COD concentration of the effluents after the pretreatments of WAO and coagulation and acidic hydrolysis. It was from 4967 to about 3000 mg/L in WAO at  $200^\circ\text{C}$  and the total pressure of 4 MPa after 150 min reaction. By using  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts, the removals of COD were respectively about 40% and 46%, which was higher than that without catalysts in the WAO. In the process of coagulation and acidic hydrolysis, the COD removal was 33.5%, visibly lower than that of CWAO over  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalyst. As shown in Fig.5, the ratio of  $\text{BOD}_5$  to COD for the different treatment methods was observed. The  $\text{BOD}_5/\text{COD}$  ratio is a very important index for any waste to be biodegradable. When the ratio is over 0.5, an industrial waste is considered as an easily biodegradable wastewater. So the  $\text{BOD}_5/\text{COD}$  ratio of the effluents pretreated with WAO and coagulation and acidic hydrolysis was investigated. In Fig.5, the  $\text{BOD}_5/\text{COD}$  ratio of the initial apramycin wastewater was only 0.31. This indicated the initial wastewater was not suitable for the biological treatment. After the WAO process without catalyst, the ratio of  $\text{BOD}_5/\text{COD}$  (about 0.46) increased at  $200^\circ\text{C}$  and 4 MPa after a 150 min reaction. It meant that the effluents

could be treated by biological treatment. However, the ratio obviously increased from 0.31 to 0.49 and 0.54 using  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts. It was 0.45 with coagulation and acidic hydrolysis. When the wastewater treated by coagulation and acidic hydrolysis was degraded with biological treatment (anaerobic and aerobic treatment) in Fig.2, COD concentration was decreased to about 560 mg/L. However, the concentration was higher than the standard of discharge laws. Apramycin had toxic to the bacteria. This resulted in that the concentration was slightly decreased. This inferred that the traditional treatment method was not effective for apramycin wastewater and the pretreatment of coagulation and acidic hydrolysis was not advantageous to biological treatment.

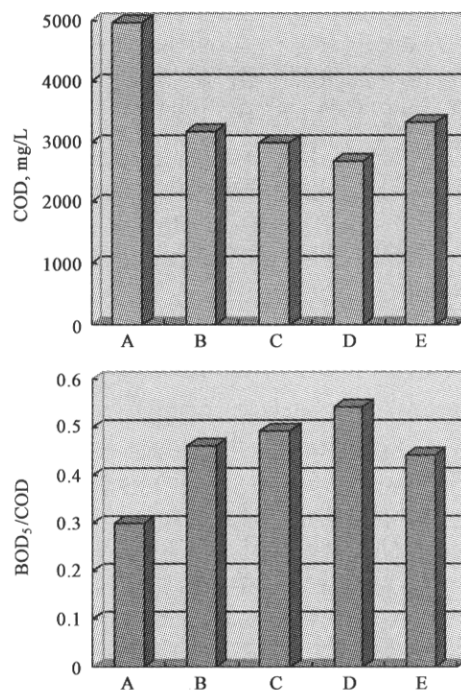


Fig.5 COD concentration and the ratio of  $\text{BOD}_5/\text{COD}$  of the effluent with the different treatment methods for apramycin wastewater

A. initial wastewater; B. WAO; C.  $\text{RuO}_2\text{-Al}_2\text{O}_3$ ; D.  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$ ; E. coagulation and acidic hydrolysis

## 2.3 Color and odor of the wastewater

The color and odor of the initial apramycin wastewater and the effluents pretreated by two methods were studied. The initial apramycin wastewater had severe odor, and was deeply brown. After the pretreatment of coagulation and acidic hydrolysis method, the color and odor was as same as the initial after 10 days run. However, in WAO the color and odor of apramycin wastewater were effectively improved. The color obviously changed from deeply brown to flaxen, and the severe odor disappeared in WAO. This meant that WAO is a hopeful treatment to the color and odor of the wastewater.

## 2.4 Stability of catalysts

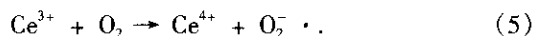
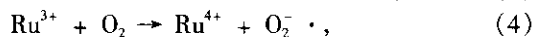
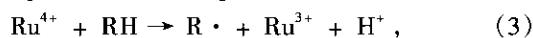
Fig. 4 and 5 indicated that  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts had good activity in WAO of apramycin wastewater. Moreover, the addition of  $\text{CeO}_2$  obviously promoted the removal of COD and apramycin, and made the  $\text{BOD}_5/\text{COD}$  ratio increase. The stability of  $\text{RuO}_2/\text{Al}_2\text{O}_3$  and  $\text{RuO}_2\text{-CeO}_2/\text{Al}_2\text{O}_3$  catalysts was investigated in WAO of apramycin wastewater. Table 1 shows that the amounts of

leaching metal ions of the two catalysts in WAO at 200°C and 4 MPa after 150 min run. As shown in Table 1, no leaching of Ru was detected, and leaching of Al ions decreased from 5.2 to 2.1 mg/L with RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in WAO of the apramycin wastewater. This indicated that the addition of CeO<sub>2</sub> promoted the stability of RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 1** The amounts of leaching metal ions of RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts in WAO at 200°C and 4 MPa after a 150 min run

Samples	Ru, mg/L	Al, mg/L
RuO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	0.3	5.2
RuO <sub>2</sub> -CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	—	2.1

WAO of organic compounds involves a free radical chain reaction in some reports (Barbier, 1998). With oxygen, the production of hydroxyl radical (HO·) is quite unlikely, but hydroperoxyl radical (HO<sub>2</sub>·) could be produced by oxygen and an organic compound RH according to the following reactions (Barbier, 1997; Rivas, 1998).



Oxygen in the liquid got an electron and formed superoxide radical (O<sub>2</sub><sup>·-</sup>) by the Reaction 1. HO<sub>2</sub>·, strong oxidative species, was produced from O<sub>2</sub><sup>·-</sup> with H<sup>+</sup> in the solution. The occurrence of HO<sub>2</sub>· was helpful to oxidize organic pollution, so the concentration of apramycin and COD obviously decreased with WAO of the apramycin wastewater. With RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, the catalytic surface areas helped the oxygen in the liquid or the gas and organic compounds to adsorb on the surface. Reaction 3 and 4 would fasten the occurrence of superoxide radical (O<sub>2</sub><sup>·-</sup>), i.e. the rate of HO<sub>2</sub>· was fasted. Hence, the removal of organic compounds was much higher with the catalysts than that without the catalyst in WAO of the apramycin wastewater. Moreover, the addition of CeO<sub>2</sub> improved oxygen to get an electron from Ce<sup>3+</sup> (in Reaction 5) and transform to superoxide radical (O<sub>2</sub><sup>·-</sup>). This would fasten the occurrence of hydroperoxyl radical (HO<sub>2</sub>·), so the removal of apramycin and COD over RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was the highest. This agrees with the results of CWAQ of the apramycin wastewater.

### 3 Conclusions

In this study, WAO and coagulation and acidic hydrolysis to treat apramycin wastewater were investigated. The removal of apramycin and COD was higher by WAO than that by coagulation and acidic hydrolysis methods. With RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, the removals of apramycin and COD were respectively 55.1% and 46.0%. The ratio of BOD<sub>5</sub>/COD was increased from 0.31 to 0.45, 0.49 and 0.54 with coagulation and acidic hydrolysis and CWAQ over RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. The biodegradability of apramycin wastewater was improved with CWAQ, but the traditional biological treatment method was not effective for

apramycin wastewater. The color and odor of the wastewater were effectively controlled and the reaction time was obviously shortened with WAO. Strong free radical chain HO<sub>2</sub>· may produce and promote organic compound oxidized during WAO of the apramycin wastewater. With RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, the rate of HO<sub>2</sub>· occurrence was fasted. And the addition of CeO<sub>2</sub> could promote the activity and stability of RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in WAO of apramycin wastewater.

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