

## Ammonia removal in the catalytic wet air oxygen process of landfill leachates with Co/Bi catalyst

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**Abstract** Oxidation of ammonia in landfill leachates in the catalytic wet air oxidation (CWAO) process was investigated with Co/Bi catalyst. The characterization of the Co/Bi catalyst was carried out by the X-ray diffraction technique. Studies of ammonia removal from the landfill leachates by CWAO showed that Co/Bi catalyst exhibited higher activities for both total organic carbon (TOC) and ammonia with removal levels of 99% for TOC and 98% for ammonia, respectively. Results also indicated that large amounts of ammonia were produced during the elimination of nitrogenous organic compounds in the CWAO process and the further oxidation of ammonia gave off essentially  $N_2$  under 240 °C. When the system temperature reached above 240 °C, ammonia oxidation rate was much higher with nitrate dominating in the effluent; a very small amount of nitrite was observed in the reaction process, it possibly acts as the intermediate of nitrate ion and molecular nitrogen formation, showing that the system temperature had significant effects on the ammonia oxidation and reaction selectivity towards the production of molecular nitrogen or nitrate.

**Keywords** Co/Bi catalyst; CWAO process; landfill leachates; nitrogen removal

### Introduction

Because of the low cost, advanced technologies, and convenience in management and transportation, the landfill has an one of the most recommendable technologies for the garbage treatment at home and abroad (Barbier *et al.*, 2002). However, large amounts of nitrogenous compounds, especially ammonia, in the leachates generated in the process of municipal landfill, would have environmentally negative effects such as eutrophication of waters and toxicity to the aquatic life (Deiber *et al.*, 1997; Cao *et al.*, 2003). Moreover, high concentration of ammonia in the leachates could inhibit microorganism activity; consequently affecting the stability and effectiveness of the biochemical treatment. Nowadays, ammonia could be removed from waste by a nitrification/denitrification biological process (Hao *et al.*, 1994; Peng *et al.*, 2000). However, this relatively cheap treatment had a low yield especially for continuous treatment, and produced high amounts of sludge (Hung *et al.*, 2003). In some conventional physical and chemical treatment processes, such as activated carbon fibre adsorption and the air stripping process, ammonia was not ultimately eliminated, only phase transformed, thus requiring further disposal (Imanura *et al.*, 1982; Li *et al.*, 2004a). Ion exchange was very effective in removing ammonia from wastewater, which was feasible only when the concentration of the ammonia was low (Li *et al.*, 2004a).

Catalytic wet air oxidation, which can eliminate organic matter without toxic by-product formation, was one of the most promising techniques for the treatment of various types of wastewater and sludge: industry wastewater as textile process effluent, sludge generated in the activated sludge processing and sewage water (Harada and Yamasaki, 1994; Oliviero *et al.*, 2003). In recent years, various catalysts have been developed to remove ammonia and other nitrogenous compounds in wet oxidation process, and some were very effective. However, transformation of all kinds of nitrogenous compounds in

the CWAO process and mechanism of ammonia oxidation are still unclear (Li *et al.*, 2004b). In previous research, Co/Bi catalyst exhibited remarkable activities for the organic carbon abatement (Qin and Aika, 1998; Oliviero *et al.*, 2003; Li *et al.*, 2004b) and catalytic wet air oxidation of landfill leachate using Co/Bi catalyst was proved to be applicable based on the cost-benefit analysis (Li *et al.*, 2006). Hence, the objective of this study is to investigate the ammonia removal and the changes in the nitrogen species on the basis of the measurement of various nitrogen fractions, and to describe the ammonia oxidation process in the CWAO process of landfill leachates with Co/Bi catalyst.

## Methods

### Catalyst preparation and characteristics

Catalyst was prepared using Cobalt (II) nitrate and Bi (II) nitrate in terms of the molar ratio of 5:1 (Rostron *et al.*, 2001). The nitrates were dissolved in concentrated nitric acid and heated to accelerate their homogeneous mixture, then dried at 85 °C and calcined for 3 h at 350 °C in a muffle furnace in order to form metal oxides. Finally, the catalyst was ground and stored in the desiccator for use.

Figure 1 shows the X-ray diffraction (XRD) pattern of the catalyst prepared.  $\text{Co}_3\text{O}_4$  was detected by XRD, which proved that  $\text{Co}_3\text{O}_4$  was formed at 350 °C. No peaks were identified for the formation of any type of  $\text{Bi}_2\text{O}_3$  in the XRD pattern of the catalyst, but XPS spectrum confirmed that element Bi existed on the surface of the catalyst and that the surface of the complex oxide was covered with a thin layer of  $\text{Bi}_2\text{O}_3$ . The catalytic properties of this kind of catalyst depend on the interaction between Bi and Co, which played an important role in catalysis. In addition, specific surface area (BET) and pore volume of Co/Bi catalyst used in this work were  $39.25 \text{ m}^2 \cdot \text{g}^{-1}$  and 0.036 ml, respectively (Li *et al.*, 2005).

### Identification of nitrogenous compounds in the leachates

Landfill leachates used in the experiments were obtained from a landfill in Shenzhen, China. The initial concentration of TOC is more than 14,000 mg/l with ammonia level of 500–600 mg/l. GC-MS (TE-5MS) was employed to identify the nitrogenous compounds in the leachates. Primary nitrogenous organic compounds in the leachates, such as isothiazole, benzothiazole, pyridine and amine, were as follows:

### Experimental procedures

The experiment was carried out in a batch reactor, which consisted of a kettle, a condenser equipped with a magnet drive, a pressure gauge, a liquid sampling, and a relief

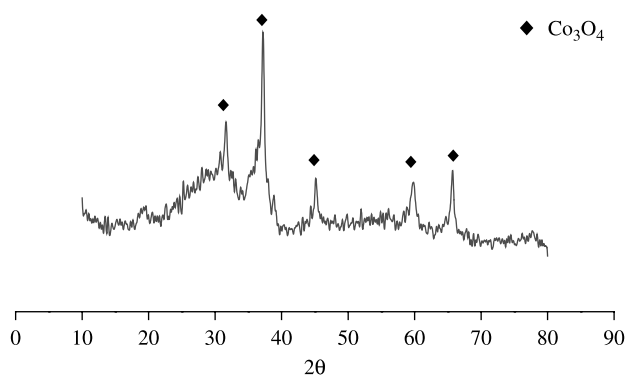


Figure 1 XRD pattern of Co/Bi catalyst

valve, etc. The schematic diagram of the experimental setup is shown in Figure 2. Before the experiments, the reactor was cleaned three or four times with distilled water. Then 0.8 litres of landfill leachates, together with the 2.67 g fresh catalysts, was charged into the reactor. Oxygen was injected into reactor to make a partial pressure at a level of  $1.0 \times 10^6$  Pa. At the desired temperatures (120, 150, 170, 190, 220, 240, 260, and 280 °C), samples in the liquid phase were collected for the measurement of mineral forms of nitrogen ( $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N,  $\text{NO}_3^-$ -N) and total nitrogen (TN).  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N and TN were measured using the methods of GB7479-87, GB7493-87 and ISO/DIS 8199 respectively. Many studies have reported that no nitrogen oxides in the vapour phase were detected in the CWAO of ammonia (Zhang, 2000; Cao et al., 2003; Li et al., 2004b), so only  $\text{N}_2$  was considered in the gas phase in this paper.

## Results and discussion

### Ammonia

In our previous work, Co/Bi catalyst exhibited remarkable activity in organic carbon abatement, and removal rate of TOC to a level of more than 99% (initial TOC level of  $> 14,000$  mg/l) was reached under laboratory conditions (Li et al., 2004b); meanwhile, in the present study, it was also found that a higher ammonia removal rate was obtained in the CWAO process of landfill leachates under the same laboratory conditions with ammonia oxidation efficiency of over 98% (initial ammonia level of  $> 500$  mg/l). This indicated that most of the total organic carbon and ammonia were simultaneously decomposed in the CWAO process of landfill leachates with Co/Bi catalyst.

### Ammonia oxidation process with the system temperature raising

Ammonia in landfill leachates was oxidized over Co/Bi catalyst in the system temperature raising process. Ammonia concentration was determined at each temperature and reported in Figure 3. In the temperature period from 120 to 280 °C, decomposition of ammonia could be divided into two stages: 120–220 °C, concentration of ammonia increased gradually and reached a maximum level of 24.03 mg/l at 220 °C, 12.49 mg/l higher than initial concentration of ammonia in the diluted landfill leachates; with the temperature increasing continually, concentration of ammonia began to decrease,

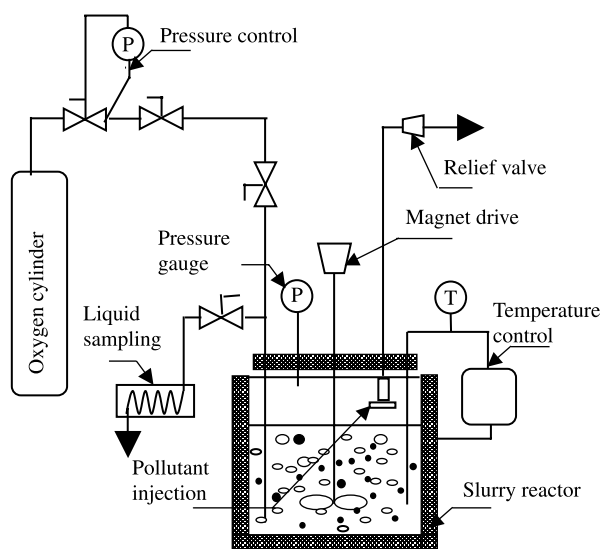
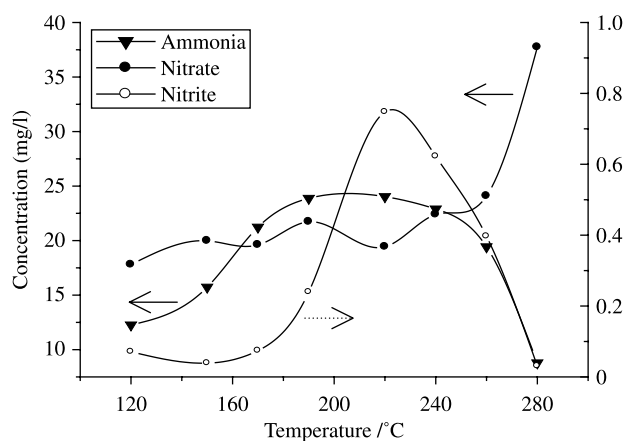


Figure 2 Schematic diagram of the experimental setup



**Figure 3** Levels of ammonia, nitrite and nitrate in the CWAO process

reaching a minimum level at 280 °C, and ammonia was notably decomposed when the temperature was higher than 240 °C.

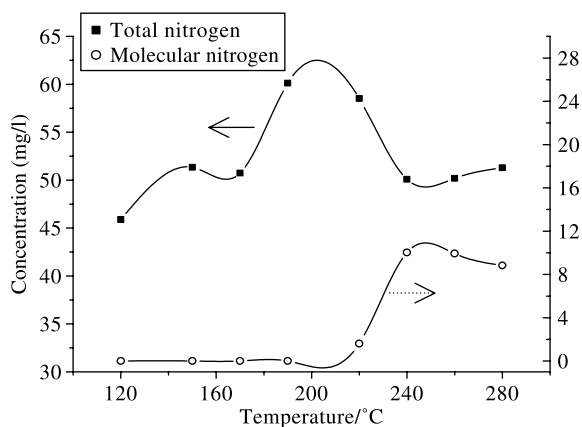
It was found that there were large amounts of nitrogenous organic compounds in the landfill leachates based on the GC-MS analysis. The N–C bond cleavage leads to formation of ammonium ions (ammonia in the alkaline solution) at a temperature range of 120 to 220 °C, and increasing of ammonia in the reaction system. At the subsequent period of 220 to 280 °C, the concentration of ammonia decreased distinctly because of the degradation of ammonia in the leachates. Concerning CWAO of nitrogenous organic compounds, some correlative research also pointed out that ammonia was the most refractory intermediate in oxidation of nitrogenous organic compounds (Zhang, 2000; Cao *et al.*, 2003; Li *et al.*, 2004b).

#### Ammonia oxidized into $\text{NO}_2^-$ -N, $\text{NO}_3^-$ -N

Mineral forms of nitrogen were only  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N,  $\text{NO}_3^-$ -N in the liquid phase, so nitrite and nitrate were tested in order to assess the production of ammonia oxidation in the CWAO process. Some of nitrite and nitrate arise in the temperature raising procedure shown in Figure 3. Levels of nitrate kept constant at the period from 120 to 240 °C, but increased rapidly along with the decomposition of ammonia, above 240 °C. From 240 to 280 °C, nitrate content was raised from 22.39 mg/l to 37.73 mg/l. Hence, it was concluded that further oxidation of ammonia was significantly oriented towards the undesirable nitrate ions when the temperature was above 240 °C. A very small amount of nitrite ion was observed, the nitrite content showed a volcano curve along with the system temperature from 120 to 280 °C in the CWAO process. After the nitrite level reached the peak, nitrate concentration increased subsequently, indicating that nitrite ions acted as the intermediate of ammonia oxidation to nitrate ions.

#### $\text{N}_2$ and TN in the CWAO process of landfill leachates

Levels of TN in the CWAO process of landfill leachates are summarized in Figure 4. At the temperature range from 120 to 200 °C, TN content increased in succession and reached the peak of 27.77 mg/l near 200 °C. In the temperature period from 200 to 240 °C, TN level began to decrease till a minimum level of 16.85 mg/l at 240 °C, and then stayed constant. Landfill leachates contained many kinds of nitrogenous compounds, some of which could not be oxidized by the method ISO/DIS 8199 under common laboratory conditions. These refractory compounds could be decomposed at high



**Figure 4** Levels of TN and  $N_2$  in the CWAO process of landfill leachates

temperature periods with high oxygen pressure on the surface of the catalyst in the reaction system, causing an accumulation of TN in the initial period. A decrease in the concentration of TN was observed at the temperature range between 200 °C and 240 °C, so it can be deduced that  $N_2$  was produced at this temperature range. Since no other nitrogenous compounds except  $N_2$ , nitrite, nitrate and ammonia were detected in the reaction system; the main product was clearly indicated to be  $N_2$  in the further oxidation. Levels of  $N_2$  obtained by the difference of TN and other nitrogen species are shown in Figure 4. A similar result was reported, but over 260 °C, when heterogeneous Mn/Ce catalyst was used in the presence of oxygen (Peng *et al.*, 2000; Zhang, 2000). In addition, Qin and Aika (1998) and Barbier *et al.* (2002) have also presented that  $N_2$  was produced in the CWAO process over  $M/Al_2O_3$  and  $M/CeO_2$  at temperature close to 200–230 °C. When the system temperature was set over 240 °C, ammonia oxidation in the CWAO process was prone to production of nitrate according to the above results. Consequently, levels of TN in the liquid phase would remain invariable when the temperature was over 240 °C.

On the basis of intermediates and end products determined, equations (1)–(10) were proposed for the CWAO process of landfill leachates with Co/Bi catalyst in this paper, which were close to the scheme reported by Barbier *et al.* (2002) as follows:



The liquid phase was maintained by high pressure in the CWAO process, so gas–liquid equilibrium of ammonia was limited and the reactions happened only in the liquid phase (Cao *et al.*, 2003). Thus, oxidation of ammonia into nitrate and  $N_2$  took place in liquid phase. The Co/Bi catalyst was required for oxidation and played an essential role in the process of ammonia oxidation with most oxidation occurring on the surface of catalyst.  $NH_2OH$  is a strong reducing agent in the alkaline leachates, which can be oxidized into  $N_2$  or HNO. Further oxidation of HNO led to the formation of  $HNO_2$ , which is not only a reducing agent but also an oxidant, and its oxidation ability, is stronger than  $HNO_3$  in the diluted solutions. When  $HNO_2$  acts as a reducing agent, its product is inevitably  $NO_3^-$ , but  $N_2$  probably appeared at low temperature (less than  $240^\circ C$ ) when  $HNO_2$ , acting as an oxidizing agent, reacted with ammonia. When the temperature was higher, an excess of oxygen species on the surface orientated the reaction towards the formation of nitrate. In conclusion, a high selectivity to molecular nitrogen was obtained when reaction (5) was faster than continual oxidation of HNO (7) and the deoxidizing reaction of  $HNO_2$  (8) was faster than oxidation reaction of it (10).

#### Effect of the system temperature on ammonia oxidation efficiency

The effect of the system temperature on ammonia oxidation efficiency was investigated and ammonia removal rates at different temperatures are shown in Figure 5. As shown in Figure 5, ammonia oxidation efficiency increased notably with increase of the system temperature. At  $220^\circ C$ , ammonia oxidation efficiency was very low, but the product of ammonia oxidation was selectively orientated towards molecular nitrogen. A fair efficiency of ammonia oxidation was obtained at temperatures ranging from  $240$  to  $280^\circ C$ , whereas the oxidation reaction has to be orientated towards the undesired product of nitrate.

Many researchers had reported that catalyst activities were enhanced and ammonia conversion rate increased with temperature (Deiber *et al.*, 1997; Qin and Aika, 1998; Cao *et al.*, 2003). Marina *et al.* pointed out that  $CH_3NH$  conversion rate increased with the temperature over Ru catalysts, but increase of temperature (above 513 K) led to a decrease of  $N_2$  (Batygina *et al.*, 2000). Li and Armor (1997) observed similar strong dependencies of  $N_2$  yield on the reaction temperature for  $NH_3$  oxidation over  $Al_2O_3$  supported Pt, Rh, and Pd catalysts at 473–633 K.

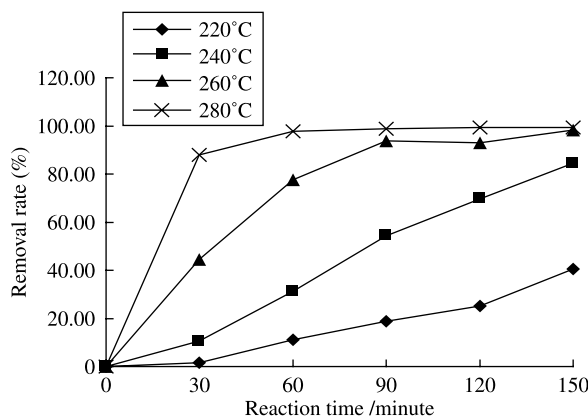


Figure 5 Effect of the system temperature on ammonia oxidation efficiency

## Conclusions

The following conclusions may be drawn based on the results of this study:

- (a) Co/Bi catalyst exhibited remarkable activities for both total organic carbon and ammonia removal with efficiencies of more than 99% for TOC and 98% for ammonia in the CWAO process of landfill leachates respectively.
- (b) Ammonia oxidation underwent three stages in the CWAO process of landfill leachates: firstly, large amounts of ammonia were produced during the decomposition of nitrogenous organic compounds in the CWAO process before 220 °C; secondly, the further oxidation of ammonia gave essentially N<sub>2</sub> via hydroxylamine in the temperature range of 220 to 240 °C; and thirdly, after the temperature was higher (over 240 °C), ammonia oxidation was much higher with the production of nitrate and nitrite ions dominating in the effluents.
- (c) The system temperature presented an important role for ammonia oxidation in the CWAO process of landfill leachates except Co/Bi catalyst.

In our further research, more reactive catalysts will be developed to improve the oxidation rate of ammonia at lower temperature, and nitrogen species in the gas phase will be measured in order to confirm the desired product N<sub>2</sub>.

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