

# Ozonation of refractory chemicals in leachate with hydrogen peroxide

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**Abstract**: Nearly 97 % of organic chemicals in Hong Kong leachate could be effectively removed by the UASB (upflow anaerobic sludge blanket) process followed by the fenton coagulation. The COD of leachate was lowered from an average of 12900 mg/L to 1440 mg/L after the UASB treatment, and was further lowered to 394 mg/L after the fenton coagulation. The remaining refractory residues could be further removed by ozonation with the addition of H<sub>2</sub>O<sub>2</sub>. The ozonation for the supernatant of the fenton coagulation was most effective at pH 7—8, with the addition of 300 mg/L of H<sub>2</sub>O<sub>2</sub>, and 30 min of reaction. The final effluent contained only 85 mg/L of COD and 10 mg/L of BOD<sub>5</sub>. On the other hand, direct ozonation of UASB effluent lowered the COD to 905 mg/L and BOD<sub>5</sub> to 103 mg/L. Ozonation improved the biodegradability of the organic residues, and also converted part of organic-N in the leachate into NH<sub>3</sub>-N and NO<sub>3</sub><sup>-</sup>-N.

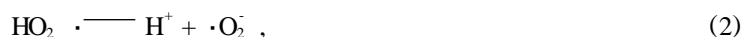
**Keywords**: biodegradability; fenton coagulation; hydrogen peroxide; leachate; ozonation; UASB

## Introduction

Hong Kong produces about 9000 tonnes of municipal solids waste daily. They are collected and disposed of at three landfill sites. The leachate from these landfills is treated on site using oxidation ponds with a hydraulic retention time (HRT) of 30 days (Chen, 1997). A recent study (Wang, 2000) demonstrated that about 90 % of COD of this leachate could be effectively reduced using the upflow anaerobic sludge blanket (UASB) process (Fang, 1993). The residual organics in the UASB effluent could then be further lowered by fenton coagulation using Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>. However, the supernatant of fenton coagulation still contained 400—500 mg/L of residual COD, which may require additional treatment in the future as regulations become increasingly stringent.

Ozonation is a widely accepted technology used for the final disinfection of water and wastewater. In recent years, it has also been increasingly used for the treatment of refractory and toxic wastewaters from various industries, such as tannery (Jochimsen, 1997), pulp and paper (Zhou, 1997), pharmaceutical (Hofl, 1997), etc., as well as landfill leachate (Primi, 1997).

The oxidation potential of ozone lies on its conversion into the free radical  $\cdot\text{OH}$  (Langlais, 1991) through a series of chain reactions as follows:



The hydroxyl radical is of high oxidation potential ( $E^0 = 2.80 \text{ V}$ ) and capable of reacting with many organic species. Peyton (Peyton, 1988) reported that  $\cdot\text{OH}$  reacts unselectively with organic substances within a millisecond.

The formation of  $\cdot\text{OH}$  is enhanced considerably by the presence of H<sub>2</sub>O<sub>2</sub>. The latter could form HO<sub>2</sub><sup>-</sup> (Reaction 6), which could react with ozone forming two free radicals, HO<sub>2</sub>· and O<sub>3</sub><sup>-</sup>· (Reaction 7), both of which are  $\cdot\text{OH}$  precursors, as shown in Reactions (2) - (5).



More importantly, the rate of forming two free radicals in Reaction (7) is about 40000 times faster than that in Reaction (1) (Gulyas, 1997). It is thus advantageous to conduct ozonation with a small dosage of  $\text{H}_2\text{O}_2$  in the treatment of both wastewater (Gulyas, 1995) and drinking water (Hirvonen, 1996).

This study was conducted to investigate the effectiveness of using ozonation with the addition of  $\text{H}_2\text{O}_2$  to further remove the refractory organic residues after the UASB and fenton coagulation treatment.

## 1 Materials and methods

### 1.1 UASB treatment

Raw leachate from a Hong Kong landfill was first treated in a 2.8-liter UASB reactor (Lau, 1997). The reactor was water-jacketed and operated at a constant temperature of 37 °C for 195 days. The HRT was kept at 6.6 days. About one liter of partially granulated sludge (26.7 g VSS/L) from a previous study plus another liter of leachate-treating activated sludge (10.8 g VSS/L) were used to seed the UASB reactor. A variable-speed peristaltic pump (Cole-Parmer, Masterflex) was used to feed raw leachate into the reactor, forcing an equal volume of supernatant out of the effluent line.

### 1.2 Fenton coagulation

The UASB effluent was then treated by the fenton coagulation process (Wang, 2000) at pH 5. The  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  dosages were 300 mg/L and 200 mg/L, respectively. After a rapid mixing to disperse the chemicals, the solution was gently mixed for 10 min for flocculation followed by 30 min of settling. The supernatant was subsequently treated by ozonation.

### 1.3 Ozonation

A stock solution containing 40 g/L of  $\text{H}_2\text{O}_2$  was prepared by diluting a 30%  $\text{H}_2\text{O}_2$  solution (Merck). Ozone was generated from oxygen using an ozonator (Osmonics, System V5-0-813). The oxygen was fed into the ozonator at 140 kPa and the voltage was controlled at 90 V. The ozonator produced a gas stream containing 52.2 mg/L of ozone. The gas bubbled through a diffuser into 500 ml of fenton coagulation supernatant containing 300 mg/ml of  $\text{H}_2\text{O}_2$  in a 2-liter reactor at room temperature. The flow rate of the ozonator gas stream was maintained at 2.4 L/min.

### 1.4 Biodegradability

The biodegradability of the organic residues in the fenton coagulation supernatant was measured according to their methanogenic and denitrification activities. The former was tested using the method of Dolfing and Bloemen (Dolfing, 1985). About 100 mg of sludge from an anaerobic leachate-treating reactor was added to each serum vial containing 100 ml of the fenton coagulation supernatant, plus nutrient, vitamins and trace metals. The pH was buffered at 7.2–7.6 using bicarbonate. The vial was placed in a 37 °C shaking bath. The amount of biogas produced and its methane content were measured daily, and the COD in the mixed liquor was measured when the test ended after 30 days. A similar test was conducted for denitrification potential of the organic residues. Denitrification sludge (100 mg) from a 2-liter sequencing batch reactor was used as seed, and 40 mg/L of nitrate was added as the electron acceptor 100 ml of fenton coagulation supernatant. The test was conducted at 20 °C also for 30 days.

### 1.5 Analytical measurements

The measurements of COD,  $\text{BOD}_5$  (5-day biochemical oxygen demand), TKN (total Kjeldahl nitrogen) and  $\text{NH}_3\text{-N}$  followed the procedures of the Standard Method (APHA, 1985). The analytical procedures of VFA followed those reported previously by Lau and Fang (Lau, 1997). Nitrate content was analyzed by an ion chromatograph (LC-10, Shimadzu) equipped with an Allsep™ anion column.

## 2 Results and discussion

### 2.1 UASB treatment of raw leachate

Raw leachate from a local landfill was treated in the UASB reactor continuously for 195 days at 37

with 66 days of HRT. The COD content in the leachate varied from 5200 mg/L to 15700 mg/L. Throughout the experiment, the pH in the reactor was pH 7.1–8.5, mainly due to the high alkalinity buffer in the leachate. After 120 days of acclimation, the reactor consistently removed 89%–91% of COD from the leachate. During days 150–195, the UASB reactor was estimated to have 27.8 g of biomass, and the leachate contained 12900 mgCOD/L and 2100 mgNH<sub>3</sub>-N/L. On average 89% of COD and 98% of BOD<sub>5</sub> were removed during this period, despite the high NH<sub>3</sub>-N content which might adversely affect the methanogenic activity (Koster, 1984). The average UASB effluent had 1440 mg/L of COD, but only 81 mg/L of BOD<sub>5</sub>. The BOD<sub>5</sub>/COD ratio was only 0.056, indicating the organic residues were recalcitrant to further biodegradation. The NH<sub>3</sub>-N concentration was increased by 8.4% after the UASB treatment because of the conversion of organic-N into NH<sub>3</sub>-N, which also resulted in an increase of pH.

## 2.2 Fenton coagulation of UASB effluent

The UASB effluent was then further treated using the fenton coagulation process. The dosages of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> were 300 mg/L and 200 mg/L, respectively. According to a recent study (Wang, 2000), H<sub>2</sub>O<sub>2</sub> and excess Fe<sup>2+</sup> synergetically removed organic residues by free-radical oxidation as well as coagulation. In this study, the fenton coagulation process removed 73% of COD from the UASB effluent, leaving 394 mg/L of COD in the effluent. Under such a condition, removing each gram of COD required 0.29 g of Fe<sup>2+</sup> and 0.19 g of H<sub>2</sub>O<sub>2</sub>, which are consistent with results of a previous study (Wang, 2000).

## 2.3 Ozonation of supernatant of fenton coagulation

Effect of H<sub>2</sub>O<sub>2</sub> dosage: A series of five ozonation experiments were conducted in parallel. The pH of the supernatant of fenton coagulation process was initially kept at pH 6. The H<sub>2</sub>O<sub>2</sub> dosage varied from nil to 500 mg/L. Fig. 1 illustrates that the H<sub>2</sub>O<sub>2</sub> dosage did not have a noticeable effect on the COD removal in the first 5 minutes. But thereafter the removal efficiency increased not only with time but also with the H<sub>2</sub>O<sub>2</sub> dosage. The COD removal efficiency began to level off at about 30 min in all experiments. Without the addition of H<sub>2</sub>O<sub>2</sub>, simple ozonation removed 23% of COD, but the efficiency increased to 32% with 300–500 mg/L of H<sub>2</sub>O<sub>2</sub>.

Since ·OH is highly reactive, the efficiency of oxidation processes often depends on the rate of ·OH generation (Haigne, 1997). Based on Reactions (6) and (7), the addition of H<sub>2</sub>O<sub>2</sub> would enhance the production of two free-radical precursors of ·OH. Thus, one would expect the COD removal efficiency would increase with the ·OH dosage, as in the cases of treating industrial wastewater (Paillard, 1988; Gulyas, 1995), and contaminated groundwater (Hirvonen, 1996). However, Fig. 1 illustrates that increasing the H<sub>2</sub>O<sub>2</sub> dosage from 300 mg/L to 500 mg/L did not improve the COD removal. This could be due to the following reaction, which shows that H<sub>2</sub>O<sub>2</sub> in excess could become an ·OH scavenger (Buxton, 1988).



It was also observed that during the first 5 min of ozonation, the gas generation was intense and the gas bubbles produced were finer than those at later stages. This could be due to the presence of surface active chemicals at the initial stage, which were degraded as ozonation proceeded (Pacana, 1982). Thus, further increase of H<sub>2</sub>O<sub>2</sub> dosage would not improve the COD removal.

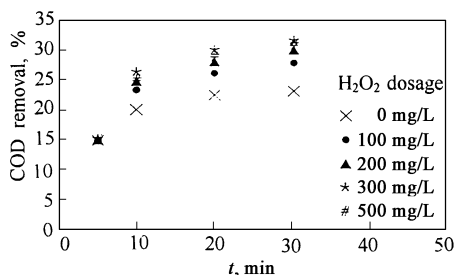
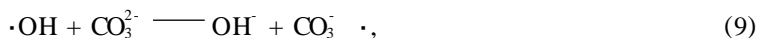


Fig. 1 Effect of duration and H<sub>2</sub>O<sub>2</sub> dosage in ozonation on COD removal of fenton-coagulation supernatant

Effect of initial pH: The effect of pH on ozonation with  $H_2O_2$  addition was unclear. Many reported that high pH is preferred for ozonation (Pacana, 1982; Singer, 1983), which is consistent with Reactions (1), (2) and (6). On the other hand, high pH also favors the formation of  $CO_3^{2-}$  and  $HCO_3^-$ , both which are scavengers of  $\cdot OH$  (Langlais, 1991) as shown in the following reactions, and thus would lower the ozonation efficiency.



In addition, low pH is favored by Reaction (4).

In order to clarify the effect of pH on ozonation, a series of experiments were conducted. In these experiments, ozonation was conducted with 300 mg/L of  $H_2O_2$  addition and lasted for 30 min. Fig. 2 illustrates that the optimal efficiency of increased drastically from 32% at pH 6 to 52% at pH 7-8; further increase of pH lowered the efficiency slightly.

#### 2.4 Ozonation of UASB effluent

Two ozonation experiments were conducted in parallel for comparison, one treating the UASB effluent and the other treating the supernatant of fenton coagulation. Both experiments were conducted at pH 7 with 500 mg/L of  $H_2O_2$  dosage and lasted for 60 min.

Results showed that ozonation removed 37% of the COD in the UASB effluent, and 68% of the COD in the supernatant of fenton coagulation. The latter was considerably higher than the 52% removal observed in the experiment which ozonation lasted only 30 min. The off-gases contained 22.4 mg  $O_3$ /L and 25.3 mg  $O_3$ /L, respectively, and the ozone concentration in both mixed liquors was 25 mg  $O_3$ /L. Therefore, based on mass balance, removing each gram of COD of the refractory organic residues in the UASB effluent consumed 16g of  $O_3$ , and corresponding  $O_3$  consumption for the fenton coagulation was 25g. The characteristics of UASB effluent before and after ozonation are listed in Table 1, along with those of the fenton-coagulation supernatant for comparison.

These results showed that 97.0% of COD of the raw leachate was removed by UASB plus fenton-coagulation, and further treatment using ozonation would improve the overall COD removal to 99.3%. The final effluent had 85 mg/L of COD and 10 mg/L of  $BOD_5$  after ozonation. On the other hand, ozonation of UASB effluent would only remove 93.0% of COD overall. Table 1 also shows that ozonation resulted in the decrease of TKN and the increase of  $NH_3$ -N. A small fraction of organic-N was oxidized to form  $NO_3$ -N.

Biodegradability of ozonation products: Table 1 shows that the  $BOD_5$ /COD ratio increased after ozonation for both the UASB effluent and the fenton-coagulation supernatant. This indicates that the biodegradability of the residual organics in both streams increased as a result of ozonation. Similar

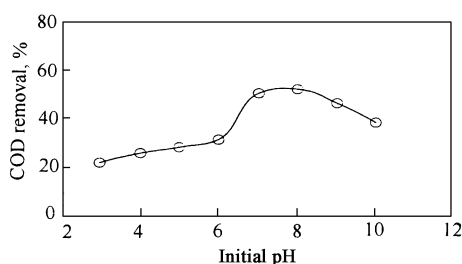


Fig. 2 Effect of initial pH on COD removal of fenton-coagulation supernatant

Table 1 Effect of ozonation on the characteristics of UASB effluent and supernatant of fenton coagulation

	UASB effluent		Supernatant of fenton coagulation	
	Before	After	Before	After
$BOD_5$ , mg/L	81	103	26	10
COD, mg/L	1440	905	394	85
$BOD_5$ /COD	0.056	0.114	0.066	0.118
TKN, mg/L	2519	2366	2497	2446
$NH_3$ -N, mg/L	2306	2320	2314	2376
Organic-N, mg/L	213	46	183	70
$NO_3$ -N, mg/L	0	25	0	22

observation had been reported by Anderson *et al.* (Anderson, 1984), and Fazzini and Young (Fazzini, 1994). This could be due to the breakdown of complex humic and aromatic substances into smaller and more biodegradable organics. Two series of experiments were conducted using the organic residues in the final effluent of the three-stage process as substrate for denitrification and anaerobic methane production. The biodegradability of the organic residues are measured by the COD removal efficiency during the tests. Fig. 3 illustrates that the organic residues were more easily degraded for denitrification than for methane production. Both activities, however, increased with the  $H_2O_2$  dosage during ozonation.

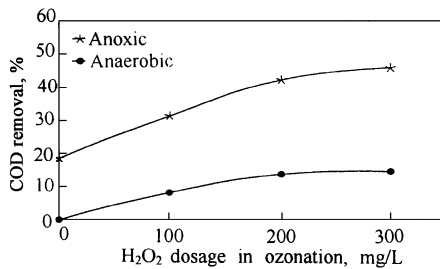


Fig. 3 Effect of  $H_2O_2$  during ozonation on biodegradability of organic residues

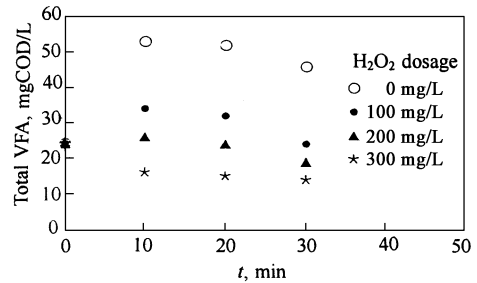


Fig. 4 Variation of total-VFA content over 30 min of ozonation at various  $H_2O_2$  dosages

Fig. 4 illustrates the change of total-VFA (as expressed in COD) at various time intervals during ozonation of the fenton-coagulation supernatant. Without the addition of  $H_2O_2$ , the total-VFA (mostly acetate and *i*-caproate) increased from 24 mgCOD/L to 53 mgCOD/L in 10 min, indicating ozonation could convert some organic residues into VFA, however, further ozonation mineralized the VFA and gradually lowered the VFA content. Also, the formation of VFA decreased with the increased dosage of  $H_2O_2$  due to strong oxidizing effect provided by the added  $H_2O_2$  which also resulted in the mineralization of VFA.

Fig. 4 also illustrates that with the addition of 300 mg/L of  $H_2O_2$  the total-VFA content was gradually decreased to 15 mgCOD/L after 30 min of ozonation. It represented merely about 18% of the organic residues which had 85 mg/L of COD as shown in Table 1. And yet Fig. 3 illustrates that nearly 50% of the organic residues could be used as substrate for denitrification. It seems that most of these substrates used for denitrification were not VFA in nature.

### 3 Conclusions

Ozonation is an effective process for the degradation of refractory organic residues in the landfill leachate. About 97.0% of 12900 mg/L of COD of the raw leachate was removed by UASB plus fenton-coagulation. Ozonation of the fenton-coagulation supernatant improved the overall COD removal efficiency to 99.3%. The final effluent had only 85 mg/L of COD and 10 mg/L of  $BOD_5$ . On the other hand, ozonation of UASB effluent removed 93.0% of COD overall. Ozonation was most effectively conducted at pH 7–8 with the addition of 300 mg/L of  $H_2O_2$  and for the duration of 30 min. Ozonation also significantly improve the biodegradability of the organic residues. Nearly 50% of these residues could be used as substrate in denitrification.

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