

Article ID: 1001-0742(2002)04-0495-06

CLC number: X703

Document code: A

Ozonation of refractory chemicals in leachate with hydrogen peroxide

WANG Peng¹, LAU W C Ivan², FANG H P Herbert²

(1. Department of Environmental Science and Engineering, Harbin Institute of Technology, Harbin 150001, China. E-mail: pwang73@yahoo.com; 2. Department of Civil Engineering, The University of Hong Kong, Hong Kong SAR, China)

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_2O_2 . 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_2O_2 , and 30 min of reaction. The final effluent contained only 85 mg/L of COD and 10 mg/L of BOD_5 . On the other hand, direct ozonation of UASB effluent lowered the COD to 905 mg/L and BOD_5 to 103 mg/L. Ozonation improved the biodegradability of the organic residues, and also converted part of organic-N in the leachate into $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$.

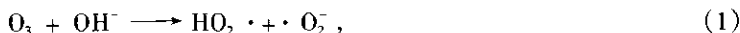
Keywords: biodegradability; fenton coagulation; hydrogen-peroxide; leachate; ozonation; UASB

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^{2+} and H_2O_2 . 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.

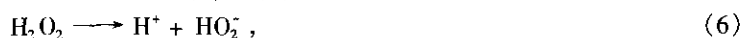
Ozonation is a widely accepted technology used for the final disinfection of water and wastewater. In recent years, it has also been increasingly used for the treatment of refractory and toxic wastewaters from various industries, such as tannery (Jochimsen, 1997), pulp and paper (Zhou, 1997), pharmaceutical (Hoff, 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_2O_2 . The latter could form HO_2^- (Reaction 6), which could react with ozone forming two free radicals, $\text{HO}_2 \cdot$ and $\cdot\text{O}_3^-$ (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 H_2O_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 H_2O_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 Fe^{2+} and H_2O_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 H_2O_2 was prepared by diluting a 30% H_2O_2 solution (Merek). 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 H_2O_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 Dolfig and Bloemen (Dolfig, 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, 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 (IC-10, Shimadzu) equipped with an AllsepTM 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°C

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 27.8g of biomass, and the leachate contained 12900 mgCOD/L and 2100 mgNH₃-N/L. On average 89% of COD and 98% of BOD₅ were removed during this period, despite the high NH₃-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 BOD₅. The BOD₅/COD ratio was only 0.056, indicating the organic residues were recalcitrant to further biodegradation. The NH₃-N concentration was increased by 8.4% after the UASB treatment because of the conversion of organic-N into NH₃-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 Fe²⁺ and H₂O₂ were 300 mg/L and 200 mg/L, respectively. According to a recent study(Wang, 2000), H₂O₂ and excess Fe²⁺ 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 394mg/L of COD in the effluent. Under such a condition, removing each gram of COD required 0.29 g of Fe²⁺ and 0.19g of H₂O₂, which are consistent with results of a previous study (Wang, 2000).

2.3 Ozonation of supernatant of fenton coagulation

Effect of H₂O₂ 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 H₂O₂ dosage varied from nil to 500 mg/L. Fig. 1 illustrates that the H₂O₂ 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 H₂O₂ dosage. The COD removal efficiency began to level off at about 30 min in all experiments. Without the addition of H₂O₂, simple ozonation removed 23% of COD, but the efficiency increased to 32% with 300—500 mg/L of H₂O₂.

Since ·OH is highly reactive, the efficiency of oxidation processes often depends on the rate of ·OH generation(Hoigne, 1997). Based on Reactions (6) and (7), the addition of H₂O₂ 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 H₂O₂ dosage from

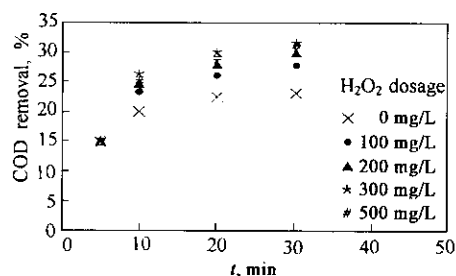


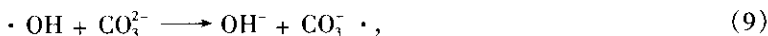
Fig.1 Effect of duration and H₂O₂ dosage in ozonation on COD removal of fenton-coagulation supernatant

300 mg/L to 500 mg/L did not improve the COD removal. This could be due to the following reaction, which shows that H₂O₂ 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 H₂O₂ dosage would not improve the COD removal.

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 $\cdot\text{OH}$ (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.

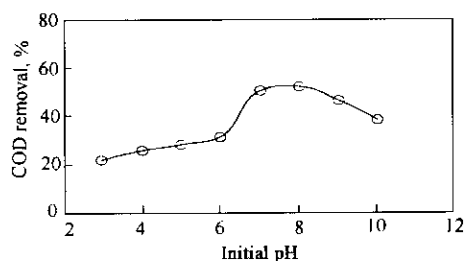


Fig. 2 Effect of initial pH on COD removal of fenton-coagulation supernatant

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 $\text{NH}_3\text{-N}$. A small fraction of organic-N was oxidized to form $\text{NO}_3\text{-N}$.

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
$\text{NH}_3\text{-N}$, mg/L	2306	2320	2314	2376
Organic-N, mg/L	213	46	183	70
$\text{NO}_3\text{-N}$, mg/L	0	25	0	22

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

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.

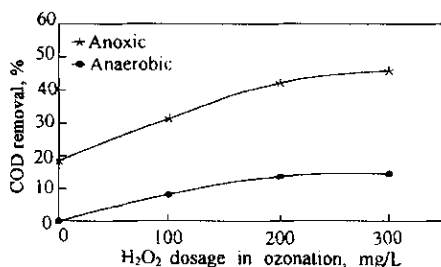


Fig. 3 Effect of H_2O_2 during ozonation on biodegradability of organic residues

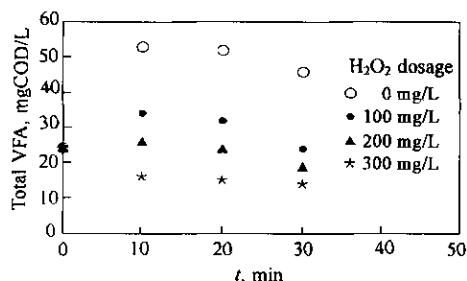


Fig. 4 Variation of total-VFA content over 30 min of ozonation at various H_2O_2 dosages

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.

Acknowledgements: The authors are grateful to the Hong Kong Research Grants Council for the partial financial support of this study, to the Croucher Foundation for granting Dr. Wang Peng the Croucher Chinese Visitorship, and to Dr. X. Y. Li for his technical assistance.

References:

Anderson C K, Saw C B, Howarth C R, 1984. Ozonolysis of wastewaters using a spinning disc reactor[C]. The 39th Purdue University

- industrial waste conference proceedings. May 8—10, USA: Purdue University. 163—172.
- APHA, 1985. Standard methods for the examination of water and wastewater[S] (16th edn.). Washington D. C.: American Public Health Association.
- Buxton G V, Greenstock C L, Helman W P *et al.*, 1988. Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in aqueous solution[J]. *J Phy Chem Ref Dat*, 17: 513—886.
- Chen T, Esnault D, Koenig A, 1997. First year operation of the NENT landfill leachate treatment works in Hong Kong[C]. Proceedings of the 6th international landfill symposium: Sardinia 97, October 13—17. Cagliari, Italy. 217—228.
- Dolling J, Bloemen W C B M, 1985. Activity measurements as a tool to characterize the microbial composition of methanogenic environment [J]. *J Microbiol Methods*, 4: 1—12.
- Fang H H P, Chui H K, 1993. Maximum COD loading capacity in UASB reactor at 37 °C [J]. *J Environ Engng, ASCE*, 119(1): 103—119.
- Fazzini L, Young J C, 1994. Use of ozone and ultraviolet oxidation to enhance the biological degradation of refractory organics in landfill leachate[C]. The 49th Purdue University industrial waste conference proceedings. USA: Purdue University. 253—262.
- Gulyas H, von Bismarck R, Hemmerling L, 1995. Treatment of industrial wastewaters with ozone/hydrogen peroxide[J]. *Wat Sci Tech*, 32 (7): 127—134.
- Hirvonen A, Tuhkanen T, Kalliokoski P, 1996. Treatment of TCD - and PCEO contaminated groundwater using UV/H₂O₂ and O₃/H₂O₂ oxidation processes[J]. *Wat Sci Tech*, 33(6): 67—73.
- Hoff C, Sigl G, Specht O *et al.*, 1997. Oxidative degradation of AOX and COD by different advanced oxidation processes: a comparison study with two samples of a pharmaceutical wastewater[J]. *Wat Sci Tech*, 35(4): 257—264.
- Hoigne J, 1997. Inter-calibration of OH radical sources and water quality parameters[J]. *Wat Sci Tech*, 35(4): 1—8.
- Jochimsen J C, Schenk H, Jekel M R *et al.*, 1997. Combined oxidative and biological treatment for separated streams of tannery wastewater [J]. *Wat Sci Tech*, 36(2—3): 209—216.
- Koster I W, Lettinga G, 1984. The influence of ammonium-nitrogen on the specific activity of pelletized methanogenic sludge[J]. *Agricultural Wastes*, 9: 205—216.
- Langlais B, Reckhow D A, Brink D R, 1991. Ozone in water treatment[M]. Application and engineering. Chelsea: Lewis Publishers.
- Lau I W C, Fang H H P, 1997. Effect of temperature shock to thermophilic granules[J]. *Wat Res*, 31(10): 2626—2632.
- Pacana M J, Guroi M D, 1982. Oxidation of dissolved organics by ozone and UV in high-strength industrial wastewater[C]. Industrial wastewater. Proceedings of the fourteenth Mid-Atlantic conference. June 27—29. 278—291.
- Pailard H, Brunet R, Dore M, 1988. Optimal conditions for applying an ozone-hydrogen peroxide oxidizing system[J]. *Wat Res*, 22(1): 91—103.
- Peyton G R, 1988. Understanding and optimizing ozone/UV treatment for the destruction of hazardous organic compounds in water: mechanism efficiency and by-product[J]. *Detoxif Hazard Wastes*, 1: 353—368.
- Primi C, Courant P, Amar D *et al.*, 1997. Leachate treatment by coupling biological nitrification-denitrification and oxidation by ozone[C]. Proceedings of 6th international landfill symposium: Sardinia 97, October 13—17. Cagliari, Italy. 211—218.
- Singer P C, Guroi M D, 1983. Dynamics of the ozonation of phenol. I. Experimental observations[J]. *Water Res*, 17: 1163—1173.
- Wang P, Lau W C, Ivan, Fang H P Herbert *et al.*, 2000. Landfill leachate treatment with combined process of UASB and fenton coagulation [J]. *J Environ Sci Health*, A35(10): 1981—1988.
- Zhou H, Smith D W, 1997. Process parameter development for ozonation of kraft pulp mill effluents[J]. *Wat Sci Tech*, 35(2—3): 251—259.

(Received for review August 22, 2001. Accepted September 27, 2001)