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## Photoassisted fenton oxidation of refractory organics in UASB-pretreated leachate

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**Abstract:** Nearly 91% of organic pollutants in Hong Kong leachate could be effectively removed by the UASB (upflow anaerobic sludge blanket) process followed by the fenton coagulation. The COD (chemical oxygen demand) of leachate was lowered from an average of 5620 mg/L to 1910 mg/L after the UASB treatment at 37°C, and was further lowered to 513 mg/L after fenton coagulation. The remaining refractory residues could be further removed by photochemical oxidation with the addition of H<sub>2</sub>O<sub>2</sub>. The BOD/COD ratio was greatly increased from 0.062 to 0.142, indicating the biodegradability of organic residues was improved. The photochemical oxidation for the fenton-coagulation supernatant was most effective at pH 3—4, with the addition of 800 mg/L of H<sub>2</sub>O<sub>2</sub>, and UV radiation time of 30 minutes. The final effluent contained only 148 mg/L of COD, 21 mg/L of BOD (biochemical oxygen demand) and 56 mg/L of TOC (total organic carbon).

**Keywords:** biodegradability; fenton; landfill leachate; photochemical oxidation; UASB

## Introduction

Anaerobic degradation of solid wastes in landfills has two distinct phases: an acidic phase followed by a methanogenic phase. Young landfills are normally operated in the acidic phase, the leachate of which contains high levels of readily biodegradable fatty acids. Mature landfills are, however, normally operated at the methanogenic phase (Chian, 1976). Leachate from such landfills has relatively lower organic strength, as anaerobes have converted fatty acids and other easily biodegradable matters into methane inside the landfill. The organic residues in such a leachate are refractory to further biodegradation. As a result, biological treatment of leachate from a mature landfill is often ineffective. Hong Kong produces about 9500 tonnes of municipal solids waste daily. They are collected and disposed of at three strategic landfill sites. Aerobic treatment of leachate is carried out on site with a hydraulic retention time (HRT) of 30 days (Chen, 1997). The process is costly because of its strong energy demand. It is, thus, warranted to develop a more cost-effective alternative.

A recent study (Wang, 2000) demonstrated that the organic content of landfill leachate could be effectively reduced using 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 500 mg/L of residual COD, which may require additional treatment in the future if regulations become more stringent.

UV radiation is a widely accepted technology used for 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. The oxidation potential of photolysis of water are based on the generation of hydroxyl radicals ( $\cdot\text{OH}$ ) from an oxidant to be added (Braun, 1997). With H<sub>2</sub>O<sub>2</sub>,  $\cdot\text{OH}$  can be produced photochemically, as shown in Reaction(1).



where, the  $\cdot\text{OH}$  is the high oxidation potential ( $E^\circ = 2.80 \text{ V}$ ) and the capable of reacting with many organic species through a series of chain reactions. Peyton (Peyton, 1988) reported that  $\cdot\text{OH}$  reacts

unselectively with organic substances within a millisecond.

Another yielding of  $\cdot\text{OH}$  can be resulted from the photolysis of hydrolytic  $\text{Fe}(\text{III})$  complex in the fenton-coagulation supernatant. Ruppert *et al.* (Ruppert, 1993) reported that  $\text{Fe}^{3+}$  can be reduced to  $\text{Fe}^{2+}$  by UV light. For example, the photolysis of  $\text{Fe}(\text{OH})^{2+}$  in an acidic solution produces ferrous ion and  $\cdot\text{OH}$  according to the following reaction (Faust, 1990).



In the presence of hydrogen peroxide,  $\text{Fe}^{2+}$  reduced is subsequently reoxidized by  $\text{H}_2\text{O}_2$  and produces new  $\cdot\text{OH}$  through the fenton reaction (Walling, 1975).



This study was conducted to investigate the effectiveness of using photochemical oxidation with the addition of  $\text{H}_2\text{O}_2$  to further remove the refractory organic residues after the UASB and fenton coagulation treatment. Also examined were the effects of initial pH and  $\text{H}_2\text{O}_2$  dosage, and the photochemical effect on the biodegradability.

## 1 Materials and methods

Raw leachate from a Hong Kong landfill was first treated in a 2.8-litre UASB reactor (Fang, 1993) with an internal diameter of 84 mm and a height of 500 mm. The reactor was water-jacketed and operated at a constant temperature of  $37^\circ\text{C}$  for 268 days. 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.

The UASB effluent was then treated by fenton coagulation process (Wang, 2000). 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 minutes for flocculation followed by 30-minute settling. The supernatant was subsequently treated by photochemical oxidation.

Experiments were carried out in a 500-ml hollow cylindrical photochemical reactor (Fig. 1) equipped with water jacket made of glass. A medium pressure mercury UV light bulb (Hanovia PC451050) with wavelength of 320 nm was positioned at the centre of the photochemical reactor and protected by another water jacket made of quartz. A standard batch experiment involved adding an appropriate volume of  $\text{H}_2\text{O}_2$  stock solution (40 g/L) prepared by diluting a 30%  $\text{H}_2\text{O}_2$  solution (Merck). Immediately after adding  $\text{H}_2\text{O}_2$ , UV light was switched on.

The measurements of COD (chemical oxygen demand), BOD (biochemical oxygen demand), and  $\text{NH}_3\text{-N}$  followed the procedures of Standard Methods (APHA, 1985). The analytical procedures of VFA (volatile fatty acids) followed those reported previously by Lau and Fang (Lau, 1997). Since residual  $\text{H}_2\text{O}_2$  would interfere COD measurement (Talinli, 1992), total organic carbon (TOC) content of many samples was also measured using a TOC analyzer (Shimadzu, TOC-5000A).

## 2 Results and discussion

### 2.1 UASB performance

Raw leachate from a local landfill was treated in the UASB reactor continuously for 268 days at  $37^\circ\text{C}$ . Table 1 summaries the characteristics of raw leachate and the UASB effluent under steady-state condition

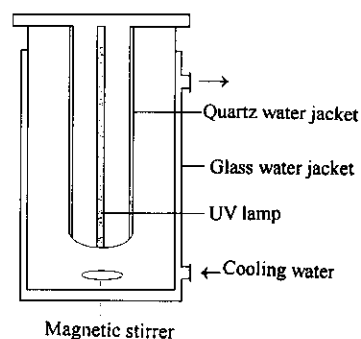


Fig. 1 Schematic diagram of photochemical reactor

during days 196–268. Within these 73 days, the UASB reactor was estimated to have 28.5g of biomass, and the average organic loading rate was 1.02g COD/(L·d) for treating leachate averaging 5626 mg COD/L and 1552 mg NH<sub>3</sub>-N/L with 5.5 days of HRT. Although high concentration of ammonia could inhibit the methanogenic activity(Koster, 1984), the UASB process on average removed 66.1% of COD, and 98% of BOD. The average UASB effluent had 1910 mg/L of COD, but only 70 mg/L of BOD. The BOD/COD ratio was only 0.037, indicating that the organic residues were recalcitrant to further biodegradation.

## 2.2 Fenton coagulation of UASB effluent

The UASB effluent was then treated using fenton coagulation process. According to a recent study (Wang, 2000), excess Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> synergetically removed organic residues by ·OH oxidation as well as coagulation. In this study, fenton coagulation process removed 73.1% of COD from the UASB effluent, leaving 513 mg/L of COD and 116 mg/L of TOC in the effluent. Under such a condition, removing

**Table 1** Characteristics of raw leachate, UASB effluent and fenton-coagulation supernatant

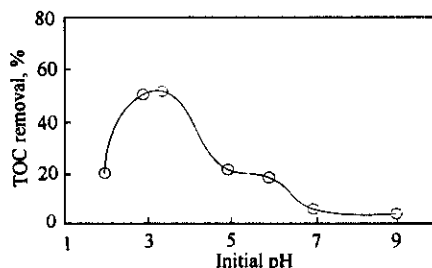
	Raw leachate	UASB effluent	Fenton-coagulation supernatant
pH	7.6 ± 0.5	8.9 ± 0.3	3.6 ± 0.2
COD, mg/L	5626 ± 470	1910 ± 140	513 ± 25
NH <sub>3</sub> -N, mg/L	1552 ± 100	1753 ± 130	1762 ± 135
BOD <sub>5</sub> , mg/L	3350 ± 160	70 ± 20	42 ± 10
TOC, mg/L	1185 ± 170	381 ± 30	116 ± 15
BOD <sub>5</sub> /COD ratio	0.595	0.037	0.062

each gram of COD required 0.22g of Fe<sup>2+</sup> and 0.14g of H<sub>2</sub>O<sub>2</sub>, which were consistent with results of two previous studies(Lau, 2000; Wang, 2000). The appearance of fenton-coagulation supernatant was found to be much clearer than the raw leachate and UASB effluent, resulting in a better transmission of UV light through the samples. Moreover, the fenton coagulation also provided enough hydrolytic Fe(III) complex in the supernatant for photolysis (Reaction (2)) and again the fenton reaction(Reaction (3)).

## 2.3 Photochemical oxidation

### 2.3.1 Effect of initial pH

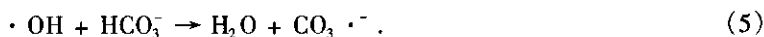
The pH value of the mixed liquor is critical to the advanced oxidation processes. It has been reported that ·OH has a higher oxidation potential at low pH and H<sub>2</sub>O<sub>2</sub> has a less tendency to decompose to form ·OH at pH greater than pH 7(Talinli, 1992). Furthermore, the concentration of inorganic carbon and the hydrolytic speciation of Fe(III) complex are strongly affected by the pH value. Therefore it is required to determine the role of pH in the photoassisted fenton reaction.



**Fig.2** Effect of initial pH on the organic removal by photochemical oxidation

Parallel experiments were conducted to determine the effect of pH using identical H<sub>2</sub>O<sub>2</sub> dosage of 800 mg/L and UV radiation time of 30 minutes. Results in Fig.2 showed that the optimal initial pH for photochemical oxidation of fenton-coagulation supernatant was pH 3–4, at which about 51.7% of TOC was removed. Only 56 mg/L of TOC remained in the final effluent. At the pH values lower and higher than this range, the organic removal was found to decline obviously. It is because high pH favors the formation of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>, both are scavengers of

·OH, as shown in the following reactions, thus lowering the photochemical efficiency.



Moreover, for the photolysis of Fe(III), the hydrolytic speciation of Fe(III) complex is very important as Fe<sup>3+</sup>, Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, and Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> have different absorption spectra and photochemical

behavior. Faust and Hoigne (Faust, 1990) reported that the hydrolytic speciation of  $\text{Fe}(\text{III})$  was dependent on the pH values and that  $\text{Fe}(\text{OH})^{2+}$  is predominant at pH 2.5—5. Pignatello (Pignatello, 1992) reported that below pH 2.8, the concentration of  $\text{Fe}(\text{OH})^{2+}$  would decline, and therefore the photoassisted fenton reaction would be retired.

When the initial pH value was adjusted to be higher than pH 6, the organic removal was drastically decreased to be less than 10% and some scale was formed on the immersion tube. The formation of scale may be the result of ferric complex precipitation (Lin, 1999). The precipitation of  $\text{Fe}^{3+}$  to amorphous oxyhydroxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) occurs at high pH, thus preventing the transmission of UV light (Pignatello, 1992). As a result, the photochemical oxidation could not take place. Therefore, the initial pH of 3.6 (i.e. the original pH value of fenton-coagulation supernatant) was chosen for the subsequent experiments.

### 2.3.2 Effect of $\text{H}_2\text{O}_2$ dosage

The effect of  $\text{H}_2\text{O}_2$  dosage on the removal of organic pollutants is illustrated in Fig. 3. The series of experiments were conducted at an initial pH of 3.6 and UV radiation time of 30 minutes. The  $\text{H}_2\text{O}_2$  dosage varied from nil to 1600 mg/L. Results in Fig. 3 showed that the COD removal efficiency increased with  $\text{H}_2\text{O}_2$  concentration up to 800 mg/L. At this concentration, the COD removal efficiency reached 71.2%, leaving 148 mg/L of COD in the UV-treated effluent. Based on Reactions (1) and (3), the addition of  $\text{H}_2\text{O}_2$  would enhance the production of  $\cdot\text{OH}$ . Thus, one would expect that the COD removal efficiency would increase with the  $\text{H}_2\text{O}_2$  dosage. However, Fig. 3 illustrates that further increase of  $\text{H}_2\text{O}_2$  dosage did not improve the COD removal. This could be due to the auto-decomposition of excess  $\text{H}_2\text{O}_2$  to oxygen and water (Reaction (6)), and the scavenging effect of  $\cdot\text{OH}$  by  $\text{H}_2\text{O}_2$  at high concentration (Buxton, 1988; Reaction (7)).



Fig. 3 also illustrates the COD removal as a function of the stoichiometric  $\text{H}_2\text{O}_2$  input percentage which was calculated by dividing the  $\text{H}_2\text{O}_2$  dosage by the COD content of sample, based on the theoretical value of 0.47g of  $\text{O}_2$  provided by each gram of  $\text{H}_2\text{O}_2$ . The diagonal line in Fig. 3 indicates the stoichiometric ratio between COD removal and the  $\text{H}_2\text{O}_2$  input. From 0% to 75% of the  $\text{H}_2\text{O}_2$  required for a stoichiometric conversion, the COD removal was higher than the theoretical value. Even without the addition of  $\text{H}_2\text{O}_2$ , the COD removal obtained was about 30%. At 9% of the stoichiometric  $\text{H}_2\text{O}_2$  input, COD was degraded about four times more than to be expected theoretically. This could be explained by the effect of additionally produced  $\cdot\text{OH}$  due to the photolysis of  $\text{Fe}(\text{III})$  hydrolytic complex (Reaction (2)).

The BOD/COD ratio of fenton-coagulation supernatant was doubled to 0.142 after photochemical oxidation. This indicates that the biodegradability of residual organics increased. It was due to the breakdown of complex humic and aromatic substances into smaller and more biodegradable organics (Fazzini, 1994).

## 3 Conclusion

About 91% of organic pollutants in Hong Kong leachate could be effectively removed by the UASB process followed by the fenton coagulation. The COD of leachate was lowered from an average of

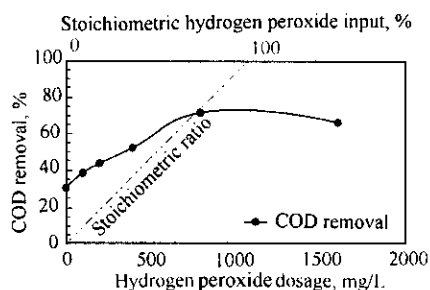


Fig. 3 Effect of  $\text{H}_2\text{O}_2$  dosage on the organic removal by photochemical oxidation

5620 mg/L to 1910 mg/L after the UASB treatment, and was further lowered to 513 mg/L after fenton coagulation. The remaining refractory residues could be further removed by photochemical oxidation with the addition of  $\text{H}_2\text{O}_2$ . The BOD/COD ratio was greatly increased from 0.062 to 0.142, indicating the biodegradability of organic residues was improved. The photochemical oxidation for the fenton-coagulation supernatant was most effective at pH 3–4, with the addition of 800 mg  $\text{H}_2\text{O}_2$ /L, and UV radiation time of 30 minutes. The final effluent contained only 148 mg/L of COD, 21 mg/L of BOD and 56 mg/L of TOC.

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