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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 H₂O₂. 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 H₂O₂, 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 Fe²⁺ and H₂O₂. 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 H₂O₂, $\cdot\text{OH}$ can be produced photochemically, as shown in Reaction (1).

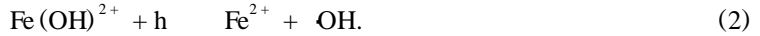


where, the $\cdot\text{OH}$ is the high oxidation potential ($E^0 = 2.80 \text{ V}$) and the capable of reacting with many organic species through a series of chain reactions. Peyton (Peyton, 1988) reported that $\cdot\text{OH}$ reacts

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unselectively with organic substances within a millisecond.

Another yielding of $\cdot\text{OH}$ can be resulted from the photolysis of hydrolytic $\text{Fe}(\text{OH})^{2+}$ complex in the fenton coagulation supernatant. Ruppert *et al.* (Ruppert, 1993) reported that Fe^{3+} can be reduced to 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, Fe^{2+} reduced is subsequently reoxidized by H_2O_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 H_2O_2 to further remove the refractory organic residues after the UASB and fenton coagulation treatment. Also examined were the effects of initial pH and H_2O_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 °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 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 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 H_2O_2 stock solution (40 g/L) prepared by diluting a 30% H_2O_2 solution (Merck). Immediately after adding H_2O_2 , UV light was switched on.

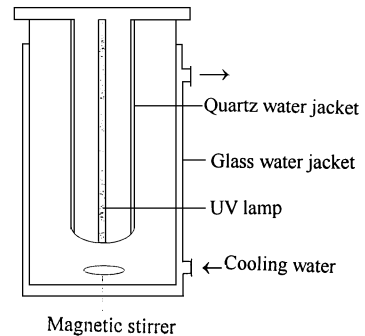


Fig. 1 Schematic diagram of photochemical reactor

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 H_2O_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 °C. Table 1 summarizes the characteristics of raw leachate and the UASB effluent under steady-state condition

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 NH₃-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 Fe²⁺ and H₂O₂ 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

each gram of COD required 0.22g of Fe²⁺ and 0.14g of H₂O₂, 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() 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 H₂O₂ 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() complex are strongly affected by the pH value. Therefore it is required to determine the role of pH in the photoassisted fenton reaction.

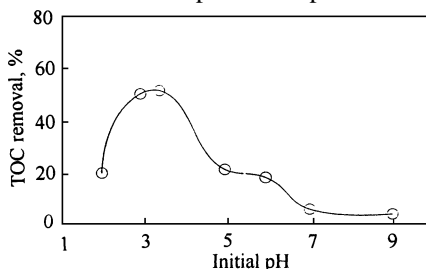


Fig. 2 Effect of initial pH on the organic removal by photochemical oxidation

Parallel experiments were conducted to determine the effect of pH using identical H₂O₂ 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 CO₃²⁻ and HCO₃⁻, both are scavengers of

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



Moreover, for the photolysis of Fe(), the hydrolytic speciation of Fe() complex is very important as Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺, and Fe₂(OH)₂⁴⁺ have different absorption spectra and photochemical

behavior. Faust and Haigne (Faust, 1990) reported that the hydrolytic speciation of $\text{Fe}(\text{OH})^{2+}$ 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 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 H_2O_2 dosage

The effect of H_2O_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 H_2O_2 dosage varied from nil to 1600 mg/L. Results in Fig. 3 showed that the COD removal efficiency increased with H_2O_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 H_2O_2 would enhance the production of $\cdot\text{OH}$. Thus, one would expect that the COD removal efficiency would increase with the H_2O_2 dosage. However, Fig. 3 illustrates that further increase of H_2O_2 dosage did not improve the COD removal. This could be due to the auto-decomposition of excess H_2O_2 into oxygen and water (Reaction (6)), and the scavenging effect of $\cdot\text{OH}$ by H_2O_2 at high concentration (Buxton, 1988; Reaction (7)).



Fig. 3 also illustrates the COD removal as a function of the stoichiometric H_2O_2 input percentage which was calculated by dividing the H_2O_2 dosage by the COD content of sample, based on the theoretical value of 0.47g of O_2 provided by each gram of H_2O_2 . The diagonal line in Fig. 3 indicates the stoichiometric ratio between COD removal and the H_2O_2 input. From 0% to 75% of the H_2O_2 required for a stoichiometric conversion, the COD removal was higher than the theoretical value. Even without the addition of H_2O_2 , the COD removal obtained was about 30%. At 9% of the stoichiometric H_2O_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 $\text{Fe}(\text{OH})^{2+}$ 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

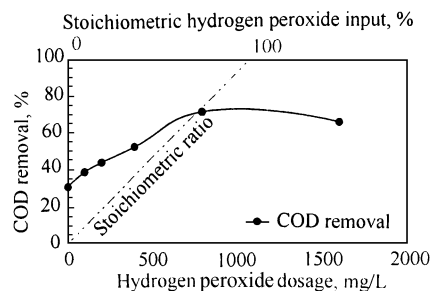


Fig. 3 Effect of H_2O_2 dosage on the organic removal by photochemical oxidation

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 H_2O_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 $\text{H}_2\text{O}_2/\text{L}$, 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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References :

- APHA, 1985. Standard methods for the examination of water and wastewater (16th Ed.) [M]. Washington D. C. : American Public Health Association.
- Braun A M, Oliveros E, 1997. How to evaluate photochemical methods for water treatment[J]. *Wat Sci Tech*, 35(4) : 17–23.
- 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 ($\cdot\text{OH}/\text{O}^\cdot$) in aqueous solution[J]. *J Phys 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]. The 6th international landfill symposium: Sardinia 97. October 13–17. Cagliari, Italy. 217–228.
- Chian E S K, Dewalle F B, 1976. Sanitary landfill leachates and their treatment [J]. *Journal of the Environmental Engineering Division, ASCE*, 103 (EE2) : 411–431.
- Fang H H P, Chui H K, 1993. Maximum COD loading capacity in UASB reactors at 37 [J]. *J Environ Eng, ASCE*, 119(1) : 103–119.
- Faust B C, Hoigne J, 1990. Photolysis of $\text{Fe}(\text{OH})_2$ -hydroxy complexes as sources of $\cdot\text{OH}$ radicals in clouds, fog and rain[J]. *Atoms Environ*, 24A(1) : 79–89.
- 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. Purdue University, U. S. A. 253–262.
- 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.
- Lau I W C, Fang H H P, 1997. Effect of temperature shock to thermophilic granules[J]. *Wat Res*, 31(10) : 2626–2632.
- Lau I W C, Wang P, Fang H H P, 2000. Ozonation of refractory chemicals in leachate with hydrogen peroxide (in press).
- Lin L S, Johnston C T, Blatchley E R, 1999. Inorganic fouling at quartz: water interfaces in ultraviolet photoreactors — . Chemical characterization[J]. *Wat Res*, 33(15) : 3321–3329.
- 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.
- Pignatello J J, 1992. Dark and photoassisted Fe^{3+} -catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide[J]. *Environ Sci Tech*, 26 : 944–951.
- Ruppert G, Bauer R, Heisler G J, 1993. The photo-fenton reaction: an effective photochemical wastewater treatment process[J]. *J Photochem Photobiol A: Chem*, 73 : 75–78.
- Talimli I, Anderson G K, 1992. Interference of hydrogen peroxide on the standard COD test[J]. *Wat Res*, 26(1) : 107–110.
- Walling C, 1975. Fenton's reagent revisited[J]. *Acc Chem Res*, 8 : 125–131.
- Wang P, Lau Ivan W C, Fang Herbert H P *et al.*, 2000. Landfill leachate treatment with combined process of UASB and fenton coagulation [J]. *J Environ Sci Health*, A35(10) : 1981–1988.

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