

ORGANIC REMOVAL OF ANAEROBICALLY TREATED LEACHATE BY FENTON COAGULATION

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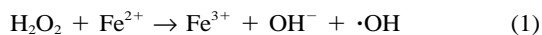
ABSTRACT: The leachate from a Hong Kong landfill, containing 15,700 mg/L of chemical oxygen demand (COD) and 2,260 mg/L of ammonia nitrogen (NH₃-N), was first treated in a UASB (upflow anaerobic sludge blanket) reactor at 37°C. The process on average removed 90.4% of COD with 6.6 days of hydraulic retention at an organic loading rate of 2.37 g of COD/L·day. The UASB effluent was further treated by the Fenton coagulation process using H₂O₂ and Fe²⁺. Under the optimal condition of 200 mg of H₂O₂/L and 300 mg of Fe²⁺/L and an initial pH of 6.0, 70% of residual COD in the UASB effluent was removed, of which 56% was removed by coagulation/precipitation and only 14% by free radical oxidation. It is obvious that H₂O₂ and Fe²⁺ had a strong synergistic effect on coagulation. The average COD in the final effluent was 447 mg/L. Removing each gram of COD required 0.28 g of Fe²⁺ and 0.18 g of H₂O₂.

INTRODUCTION

Anaerobic degradation of solid wastes in a landfill has two distinct phases: an acidic phase followed by a methanogenic phase. Young landfills normally operate in the acidic phase, the leachate of which contains high levels of readily biodegradable fatty acids. Mature landfills, however, normally operate at a methanogenic phase. Leachate from such landfills has relatively lower organic strength, because anaerobes have converted fatty acids and other easily biodegradable substances into methane inside the landfill. The organic residues in such a leachate are refractory to further biodegradation, and thus biological treatment of leachate from a mature landfill is often ineffective. Hong Kong produces over 9,000 tons of municipal solid waste daily. All the wastes are collected and disposed of at three landfill sites. The leachate is presently treated in oxidation ponds on site with a hydraulic retention time (HRT) of 30 days (Chen et al. 1997). The process is costly because of its strong energy demand. It is warranted to develop a more cost-effective alternative.

This study was conducted to develop a two-stage process for the effective treatment of Hong Kong's landfill leachate. At first, organics in raw leachate were degraded using the upflow anaerobic sludge blanket (UASB) process. Because the UASB effluent was of a colloidal nature, the Fenton coagulation process was used to further remove organic residues. The UASB process has been successfully commercialized in the past decade for the treatment of wastewater from various industries. The process was effective in degrading organic chemicals of different natures, including not just fatty acids (Fang et al. 1995) and starch (Fang and Kwong 1995) but also refractory proteins (Fang et al. 1994) and even aromatics (Li et al. 1995).

In the Fenton process (Walling 1975), ferrous ion reacts with hydrogen peroxide, producing hydroxyl radical ·OH as follows:



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The ·OH free radical, having a very high oxidation potential ($E^\circ = 2.80 \text{ V}$), is capable of reacting with many organic species through a series of chain reactions (Tyre et al. 1991). Peyton (1988) reported that ·OH reacts unselectively within a millisecond with organic substances. In this study, it was demonstrated that H₂O₂ and Fe²⁺ also had a synergistic effect on the removal of colloidal organic residues by coagulation. Effects of initial pH and the optimal dosages of Fe²⁺ and H₂O₂ were determined.

MATERIALS AND METHODS

USAB Process

Raw leachate from a Hong Kong landfill was first treated in a 2.8-L UASB reactor (Fang et al. 1995) for 6.6 days with HRT. The leachate on average had a pH of 7.7, chemical oxygen demand (COD) of 15,700 mg/L, and 2,260 mg/L of ammonia nitrogen (NH₃-N). The reactor was seeded with 1 L each of UASB sludge (26.7 g/L) and settled sludge (10.8 g/L) from a leachate-treating oxidation pond at the landfill site. The UASB seed sludge was from previous studies treating wastewater containing proteinaceous and carbohydrate pollutants. The UASB reactor in this study was water-jacketed and operated at a constant temperature of 37°C for 150 days.

Fenton Coagulation

An aqueous H₂O₂ stock solution (40 of H₂O₂/L) was prepared from a 30% H₂O₂ solution (Merck Chemical Co.). A solution of 20 g of Fe²⁺/L was prepared by dissolving FeSO₄·7H₂O (Aldrich Chemical Co.) in 0.1 M H₂SO₄. In conducting the Fenton coagulation process, the pH of the UASB effluent was first adjusted. The Fe²⁺ and H₂O₂ solutions were then added, followed by a 30-second rapid mixing. The sample was then gently stirred at 80 rpm using a Jar Tester (Phipps and Bird). After 10 minutes of flocculation, the sample was transferred to an Imhoff cone for settling. Supernatant and settled sludge were sampled for analysis after 30 minutes of settling.

Analysis

The measurements of COD, BOD₅ (5-day biochemical oxygen demand), NH₃-N and volatile suspended solids (VSS) followed the procedures of the *Standard Methods* (APHA 1998). Because residual H₂O₂ would interfere with the COD measurement (Kuo 1992; Talinli and Anderson 1992; Kang et al. 1999), the total organic carbon (TOC) content was measured using a TOC analyzer (Shimadzu, TOC-5000A).

TABLE 1. Characteristics of Raw Leachate and UASB Effluent

Characteristics	Raw leachate	UASB effluent
pH	7.7 ± 0.3	8.5 ± 0.2
COD (mg/L)	15,700 ± 1,700	1,500 ± 160
BOD ₅ (mg/L)	4,200 ± 230	75 ± 20
TOC (mg/L)	4,600 ± 150	470 ± 140
NH ₃ -N (mg/L)	2,260 ± 230	2,540 ± 250

RESULTS AND DISCUSSION

UASB Treatment

Steady state was reached in the UASB reactor after 120 days of operation. Table 1 summarizes the characteristics of raw leachate and the UASB effluent in days 120–150. During this period, the 2.8-L reactor contained 25.53 g of VSS, and the leachate contained 15,700 mg of COD/L and 2,260 mg of NH₃-N/L. With 6.6 days of HRT and an organic loading rate of 2.37 g of COD/L·day, the UASB process on average removed 90.4% of COD, 89.8% of TOC, and 98.2% of BOD₅. The UASB effluent, having a BOD₅/COD ratio of 0.05, was recalcitrant to further biodegradation. The NH₃-N concentration was increased by 12% after the UASB treatment because of the conversion of organic N into NH₃-N. This also resulted in an increase of pH, as shown in Table 1. The UASB effluent on average contained 1,500 mg/L of COD, 75 mg/L of BOD₅, and 470 mg/L of TOC. The effluent was collected during days 120–150 for the subsequent treatment of the Fenton coagulation.

Fenton Coagulation

Effect of Initial pH

According to (1), low pH favors the production of free radical ·OH (Zepp 1992). On the other hand, at high pH, H₂O₂ has a lesser tendency to form free radicals, and the production of radical ·OH is favored (Talinli and Anderson 1992; Kuo 1992). A series of preliminary experiments was conducted at a pH ranging from 2 to 9 to determine the optimal initial pH. At dosages of 200 mg of H₂O₂/L and 300 mg of Fe²⁺/L, results indicated that pH 4–6 was the optimal initial pH for the Fenton coagulation of UASB effluent. At pH 7–9, the COD reduction was unsatisfactory. On the other hand, at pH < 4, flocculation of colloidal matter was severely suppressed, also resulting in the deterioration of COD reduction. Most of the colloids carried negative charges because of the dissociation of acidic functional groups. At low pH, these functional groups become undissociated, and the negative charges are neutralized. As a result, the colloidal organics remain suspended in solution, as evidenced by the dark color of the supernatant. On the basis of these observations, pH 6 was chosen as the initial pH for all the subsequent experiments investigating the effects of Fe²⁺ and H₂O₂ dosages.

Effect of Fe²⁺ Dosage

The effect of Fe²⁺ dosage on the removal of organic residues in the UASB effluent was investigated. Experiments were conducted by dosing 200 mg/L of H₂O₂ at initial pH 6. Results in Fig. 1 illustrate that without the addition of Fe²⁺, H₂O₂ oxidized only 8% of organics. The TOC removal efficiency increased with Fe²⁺ dosage and leveled off at 60% when the Fe²⁺ dosage was 300 mg/L or more. The addition of Fe²⁺ over 300 mg/L did not increase the organic removal, probably due to the recombination of ·OH with the overdosage of Fe²⁺ (Walling 1975), as shown in (2).

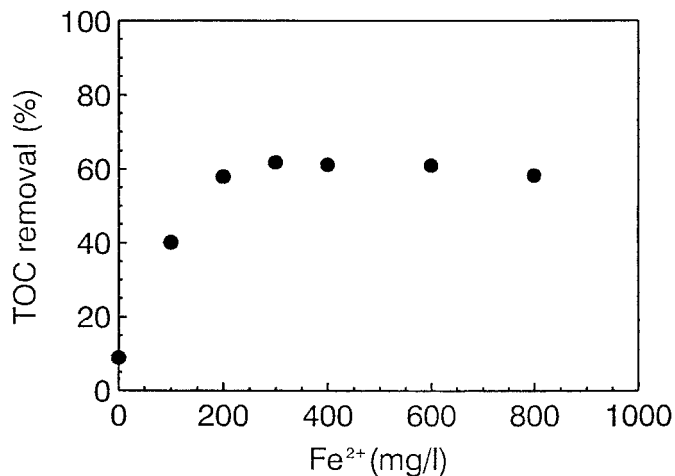
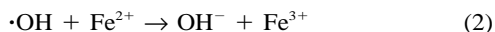
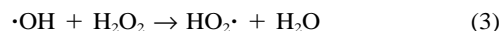


FIG. 1. Effect of Fe²⁺ Dosage in Tests at Initial pH of 6 Using 200 mg of H₂O₂/L

As a result, Fe²⁺ dosage was fixed at 300 mg/L for subsequent experiments.

Effect of H₂O₂ Dosage

Fig. 2 illustrates the effect of H₂O₂ dosage on the removal of organic pollutants. One series of experiments was conducted by dosing 300 mg of Fe²⁺/L at initial pH 6. Fig. 2 illustrates that the TOC removal efficiency increased with H₂O₂ concentration up to 300 mg/L, as reported by Kim and Huh (1997) and Yoo et al. (1997). At this concentration, the TOC removal efficiency reached 68%. A further increase of H₂O₂ dosage did not increase the TOC removal efficiency. This could be due to the scavenging of ·OH by H₂O₂ at high concentrations (Buxton et al. 1988), as shown in the following reaction:



In addition, dosing 800 mg/L or more of H₂O₂ resulted in sludge flotation. This could be due to the autodecomposition of H₂O₂. The process produced O₂, which could be trapped in the sludge matrix, causing the sludge to float.

Another series of experiments was conducted in parallel using 800 mg/L of Fe²⁺ and H₂O₂ ranging from 100 to 800 mg/L. Results are similar to those using 300 mg/L of Fe²⁺, as illustrated in Fig. 2. The extra dosage of Fe²⁺ did not appear

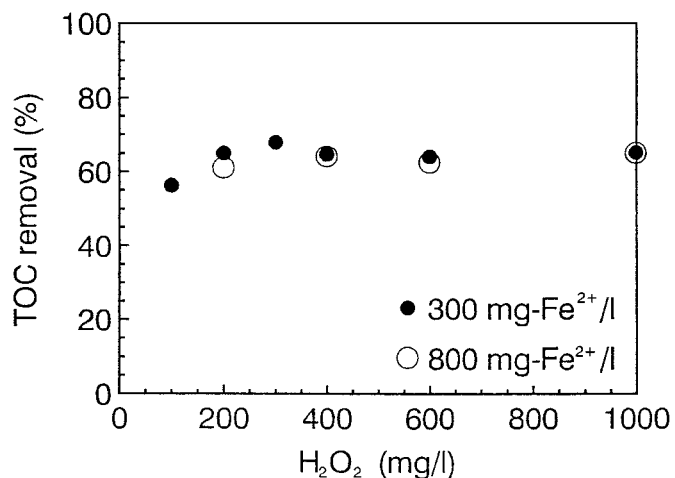


FIG. 2. Effect of H₂O₂ Dosage in Tests at Initial pH of 6 Using 300 and 800 mg of Fe²⁺/L

TABLE 2. Fenton Reagent Dosage and COD Removal

	COD (mg/L)	Reagent Dosage		COD removal (%)	Reagent Consumed		Reference
		Fe ²⁺ (mg/L)	H ₂ O ₂ (mg/L)		Fe ²⁺ (g/g of COD)	H ₂ O ₂ (g/g of COD)	
Leachate/wastewater							
Leachate pretreated by:							
UASB	1,500	300	200	70	0.28	0.18	Present study
Anaerobic-aerobic process	1,100	900	900	63	1.30	1.30	Bae et al. 1997
Aerobic process	1,720	700	200	60	0.68	0.18	Gau and Chang 1996
UASB	n/a	1,500	1,500	35	n/a	n/a	Yoo et al. 1997
Raw leachate	2,000	200	1,500	68	0.15	1.10	Kim and Huh 1997
Aromatic amines effluent	1,190	100	1,700	>95	0.09	1.50	Casero et al. 1997
Textile effluent	250	200	200	78	1.03	1.03	Kang and Chang 1997

to have any benefit in TOC removal. This again could be due to the recombination of ·OH with the overdosage of Fe²⁺ (Walling 1975), as shown in (2).

COD Reduction and Comparison with Literature Data

On the basis of these results, the optimal dosages were identified as 200 mg of H₂O₂/L and 300 mg of Fe²⁺/L. Four separated experiments were then conducted under this condition, treating the UASB effluent with 1,500 mg/L of COD. The final effluent after Fenton coagulation treatment averaged 447 mg/L of COD, corresponding to 70.0% removal efficiency. Table 2 summarizes related data in the literature for comparison. It shows that COD removal was more effective by using Fenton coagulation than those reported by others. To remove 1 g of COD in this study required only 0.28 g of Fe²⁺ and 0.18 g of H₂O₂, considerably lower than the corresponding consumptions reported by others, as shown in Table 2.

Synergetic Effect of Fe²⁺ and H₂O₂

Results of the four experiments conducted with the optimum dosages of 200 mg of H₂O₂/L and 300 mg of Fe²⁺/L showed that the Fenton coagulation process removed 1,053 mg/L of COD from the UASB effluent; of which, 840 mg/L of COD was found in the settled sludge and only 213 mg/L of COD was oxidized. Because the 200 mg/L of H₂O₂ dosed can only oxidize a maximum of 94 mg/L of COD by converting to O₂ via autodecomposition, the 213 mg/L of COD reduction was evidently caused by the oxidation by free radical ·OH. On the other hand, it was surprising to find that free radical oxidation was only responsible for 20.2% of the COD reduction; whereas, coagulation removed 79.8% of COD in the form of settled sludge. It appears that Fe²⁺ and H₂O₂ had a strong synergistic effect on the coagulation of organic residues in the UASB effluent.

Four additional experiments were conducted to evaluate the synergistic effect of Fe²⁺ and H₂O₂. Efficiencies of removing COD from UASB effluent were compared by dosing: (1) 300 mg/L of Fe²⁺; (2) 300 mg/L of Fe³⁺; (3) 200 mg/L of H₂O₂; and (4) 200 mg/L of H₂O₂ plus 300 mg/L of Fe³⁺. The first and second experiments were to evaluate the effects of Fe²⁺ and Fe³⁺ on COD reduction by coagulation alone. Results showed that dosing 300 mg/L of Fe²⁺ had little effect on reducing the COD of the UASB effluent, and dosing 300 mg/L of Fe³⁺ reduced 7.0% of COD. The superior coagulation performance of Fe³⁺ is expected because of its higher valency. The third experiment was to evaluate COD reduction by H₂O₂ oxidation alone. Results showed that dosing 200 mg/L of H₂O₂ reduced only 4.6% of COD. Lastly, the fourth experiment was to evaluate the combined effects of H₂O₂ oxidation and Fe³⁺ coagulation. Results showed that dosing 200 mg/L of H₂O₂ and 300 mg/L of Fe³⁺ only removed 8.2% of COD.

The COD removal efficiencies under these four conditions

were all substantially lower than the 70% observed in the Fenton coagulation process by dosing 200 mg/L of H₂O₂ and 300 mg/L of Fe²⁺. It is apparent that H₂O₂ and Fe²⁺ had a strong synergistic effect on enhancing coagulation of organic residues in UASB effluent. The mechanism for the drastic increase in coagulation efficiency is unclear. A further study of this matter is warranted.

CONCLUSIONS

The UASB process was able to remove over 90% of COD in the leachate, which contained 15,700 mg/L of COD and 2,260 mg/L of NH₃-N, with 6.6 days of HRT. About 70% of the residual COD in the UASB effluent could be further reduced by the Fenton coagulation process, using H₂O₂ (200 mg/L) and Fe²⁺ (300 mg/L) at initial pH 6. Oxidation was responsible for only 14% of COD reduction, and the remaining 56% was reduced by coagulation. There was a strong synergistic effect by H₂O₂ and Fe²⁺ on the coagulation of organic residues. The average COD in the final effluent was 447 mg/L.

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