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# Hydrogen peroxide-enhanced iron-mediated aeration for the treatment of mature landfill leachate

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#### Abstract

Municipal landfill leachate is being disallowed for biological treatment by some sewer authorities due to its recalcitrance and corrosiveness, and therefore physicochemical treatment may be needed. In this paper, hydrogen peroxide-enhanced iron (Fe<sup>0</sup>)-mediated aeration (IMA) was studied as an alternative for the treatment of mature landfill leachate. Bench-scale Taguchi array screening tests and full factorial tests were conducted. Iron grade, initial pH, H<sub>2</sub>O<sub>2</sub> addition rate, and aeration rate significantly influenced both overall chemical oxygen demand (COD) removal and iron consumption. In the enhanced IMA-treated leachate at an initial pH of 8.2, COD was reduced by 50% due to oxidation and coagulation, a level almost equivalent to those obtained by Fenton treatment. Meanwhile, the 5-day biochemical oxygen demand (BOD<sub>5</sub>)/COD ratio was increased from 0.02 to 0.17. In particular, the effect of initial pH became minor at H<sub>2</sub>O<sub>2</sub> addition rate greater than the theoretical demand for complete oxidation of organics by H<sub>2</sub>O<sub>2</sub>. In addition, 83% of 300 mg/L ammonia nitrogen and 38% of 8.30 mS/cm electrical conductivity were removed when the initial pH was not adjusted. Based on these results, the process appears suitable for treatment of mature leachate. © 2007 Elsevier B.V. All rights reserved.

Keywords: Coagulation; Iron; Landfill leachate; Oxidation; Recalcitrant organics

# 1. Introduction

Landfill leachates produced from sanitary landfills ought to be properly managed or treated; otherwise it can permeate ground water or mix with surface waters and cause the pollution of soil, ground water, and surface water. Organic constituents, ammonia, and heavy metals/metalloids are three principal issues with regard to the treatment and disposal of leachates. Landfill leachates are often disposed to municipal sewers, where available. However, mature leachate characterized by low BOD<sub>5</sub>/COD ratio (<0.3) and a high fraction of high molecular-weight organics is particularly challenging due to low biodegradable fraction of the organics and constituent toxicity to biological process. For example, in the case of activated sludge treatment, corrosion of the pump station, unstable chlorine residual in the treatment plant effluent, and sludge bulking

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and settling problems have been issues [1]. Hence, physicochemical processes may be required for pretreatment or full treatment of such leachate.

Since the 1970s, physicochemical methods including flocculation/precipitation [2,3], activated carbon adsorption [4], and chemical oxidation [5–9] have been investigated for treatment of mature leachate. However, most of these technologies focus on reduction of organic constituents; and the additional treatments are often required for removal of ammonia nitrogen and heavy metals/metalloids. For example, Fenton oxidation is essentially ineffective to remove ammonia [1,10–12], and may cause increase of total dissolved solids (TDS) in effluent [2], though it is able to efficiently oxidize organic components.

Recently, the oxidation of EDTA and glyoxylic acid, and coprecipitation of metal cations from water by iron (Fe<sup>0</sup>)-mediated aeration (IMA), where molecular oxygen (O<sub>2</sub>) is activated by Fe<sup>0</sup>, have been shown [13–15]. The oxidative mechanism of the IMA process at acidic condition may be related to generation of hydroxyl radicals through the well-known Fenton chemistry involving Fe<sup>II</sup> and intermediately generated H<sub>2</sub>O<sub>2</sub>. However,

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the mechanism of organics oxidation at neutral-weakly basic pH has not been known to be general. Englehardt et al. [14] suggested production of other reactive species such as ferryl under such conditions, which involves Fe<sup>II</sup>-mediated H<sub>2</sub>O<sub>2</sub> formation. Furthermore, iron oxyhydroxides produced can precipitate a number of heavy metals such as Cd<sup>2+</sup> and Pb<sup>2+</sup>. Additionally, other workers [16,17] suggested the importance of non-hydroxyl radical oxidants such as ferryl in a similar reaction system at neutral pH through hydroxyl radical scavenger tests. Of note, in the postulated pathways to generate whether hydroxyl radicals or ferryl, the  $Fe^{II}$ -mediated  $H_2O_2$  formation is a key step to subsequent production of oxidants. Therefore, we hypothesize that direct introduction of H2O2 to IMA process can enhance the production of the oxidants, whether hydroxyl radicals or other reactive oxidative species. On the other hand, the iron sludge produced during the process, the corrosion products of  $Fe^{0}$ , is expected to remove some inorganic pollutants (e.g., co-precipitation of heavy metals), and air bubbling, as the O<sub>2</sub> introduction method, also may reduce the content of ammonia nitrogen if pH is controlled within a proper range.

The aim of this paper is to investigate the feasibility of application of this  $H_2O_2$ -enhanced iron-mediated aeration process for treatment of mature landfill leachate. Effects of iron grade, initial pH,  $H_2O_2$  addition rates, and aeration rates on reduction of organic constitutes and iron consumption were assessed through a group of Taguchi array experiments. The contributions of oxidation and coagulation to reduction of organic constituents, and the mode of  $H_2O_2$  addition were evaluated through full factorial tests. In addition, the removal rates of ammonia nitrogen, and electrical conductivity from the mature leachate were investigated.

#### 2. Experimental

#### 2.1. Landfill leachate and reagents

Landfill leachate was collected from North Central Landfill in Polk County (Winter Haven, FL). The average composition of the tested landfill leachate COD were as follows: COD, 1200–1300 mg/L; electrical conductivity, 8.30 mS/cm; ammonia nitrogen, 300 mg/L; and pH, 8.2. Noticeably, the mean BOD<sub>5</sub>/COD was 0.02, typical of mature leachate. The leachate was collected in a zero headspace plastic bottle and refrigerated at 4 °C until use. Grade 0000 and grade 3 fibrous iron (Fe<sup>0</sup>) (Homax Products, Bellingham, WA), as well as Brillo<sup>®</sup> fibrous iron (Fe<sup>0</sup>) (Church & Dwight Co., Princeton, NJ) were used as reactive iron media ( $\rho \approx 7.8$  g/cm<sup>3</sup>). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, VWR, West Chester, PA) was purchased and used as a 30% (w/w) solution.

#### 2.2. Experimental setup

The  $H_2O_2$ -enhanced iron-mediated aeration (IMA) process using fibrous media was tested in fixed bed reactors developed by Englehardt et al. [13,14], as shown in Fig. 1. Fibrous iron was rinsed with hexane (Aldrich Chemical Co., Milwaukee, WI) to remove surface oils, dried completely, rinsed with 0.1N HCl,



Fig. 1. Iron-mediated aeration (IMA) fixed bed reactor.

and dried again. Subsequently, 0.68 g of fibrous iron was formed to a relatively uniform fiber density in a 30 mL test tube. The nominal surfaces areas of Fe<sup>0</sup> for fine Homax<sup>®</sup>, Brillo<sup>®</sup>, and coarse Homax<sup>®</sup> were 0.76, 0.48, and 0.42 m<sup>2</sup>/L, respectively. A glass tube was then inserted in the center of fibrous iron. Seventeen militers of leachate sample was dispensed to the test tube, and humidified air was delivered to the sample in the reactor through a glass capillary tube (50  $\mu$ L microcapillary tubing, Coming Glass Works, Big Flats, NY) inserted into the first glass tube. Air was delivered through the capillary tube, serving to pump water upwards through the annular space inside the first tube. Simultaneously, aeration was accomplished. Water then circulated down between walls of the first glass tube and the test tube, passing through a reaction zone containing the clean fibrous iron. Homogenous circulation in the reactor was verified in previous work [13].

#### 2.3. Experimental procedure and sample preparation

In a typical run, the desired amount of H<sub>2</sub>O<sub>2</sub> was first pippeted to the IMA fixed bed reactor. Samples were continuously aerated and circulated in the reactor. In the special case of no aeration samples were mixed by vertical shaking for 10s every 2 min for the first 30 min, for 10 s every 5 min for the second 30 min, for 10 s every hour for the remaining reaction time. At the designated sampling time, aeration was stopped, and remaining fibrous iron media, capillary tube, and inside tube were removed. The media was pressed to discharge-absorbed sample. Residual particles of  $Fe^0$  in sample were removed magnetically, and the sample was shaken. In the Taguchi array experiments and tests for removal of ammonia nitrogen and electrical conductivity, total iron consumption was measured as follows. An aliquot of this homogenized solution (mixture of iron sludge and leachate sample) was pipetted to a glass bottle, and then completely digested through addition of concentrated nitric acid (HNO<sub>3</sub>, 69%, FishChemical, Fair Lawn, NJ). The digested solution was diluted 500:1 with deionzed water, and vacuum filtered through 0.45 µm Millipore filter membranes (#HAWP 025 00, Millipore, Bedford, MA). The filtrate was prepared for analysis for total iron, to monitor iron consumption in the reactor. In the experiments to investigate COD oxidation and coagulation, the effect of stepwise addition of H<sub>2</sub>O<sub>2</sub>, and 3D analysis of COD removal versus initial pH and H<sub>2</sub>O<sub>2</sub> dose, the amount of ferrous iron present in iron sludge produced during IMA was estimated as follows. Diluted HCl solution (2%, v/v) was continuously added to another aliquot of this homogenized solution until the iron sludge was completely dissolved. The ferrous ion in the diluted solution was measured to estimate ferrous concentration in the sludge. The remaining homogenized solution was transferred to a 10 mL graduated cylinder for a 2 h sedimentation period. The COD of sludge phase was tested and corrected based on measured concentration of ferrous ion in the sludge, and the total volume of iron sludge was measured to determine COD removed by coagulation. The upper supernatant was then vacuum filtered through 0.45 µm Millipore filter membranes to determine total COD removal efficiency. Electrical conductivity, COD, BOD<sub>5</sub>, and ammonia nitrogen of the filtrate were tested.

#### 2.4. Analytical methods

BOD<sub>5</sub> was measured according to standard method 5210 B [18]. COD was measured colorimetrically using COD digestion vials (high range, 20–1500 mg/L, HACH, Loveland, CO). Ferrous ion was measured according to standard method 3500-Fe D [18]. H<sub>2</sub>O<sub>2</sub> was measured by the titrimetric method [19]. Total iron was measured by flame atomic adsorption spectrometry (Analyst 800, Perkin-Elmer). Electrical conductivity was measured by a digital conductivity meter (Model 4081, Amber Science Inc., Eugene, OR, USA). Ammonia nitrogen was measured according to standard method 3500-NH<sub>3</sub> F [18]. Error bars in the figures represent one standard deviation (n = 3).

# 3. Results and discussion

#### 3.1. Taguchi array experiment

An orthogonal array experimental design method advocated by Taguchi [20] was used to screen for the influences of operating factors on COD removal efficiency in H<sub>2</sub>O<sub>2</sub>-enhanced IMA treatment of the landfill leachate. Four operating factors, including iron grade, initial pH, H<sub>2</sub>O<sub>2</sub> addition rate and aeration rate, were studied using fibrous IMA fixed bed reactors. In the orthogonal array, H<sub>2</sub>O<sub>2</sub> addition rate is defined as the mass ratio of peroxide concentration to 2.125 times COD<sub>0</sub>, in which COD<sub>0</sub> indicates initial COD in the leachate. This H<sub>2</sub>O<sub>2</sub> addition rate means the mass ratio of actual peroxide concentration to peroxide concentration theoretically required to oxidize COD<sub>0</sub>. The levels of each operating factor studied, and the design matrix of the L<sub>9</sub>(3<sup>4</sup>) orthogonal array are summarized in Tables 1 and 2. Characteristic values used in this experimental design were the overall COD removal efficiency and iron consumption.

The analysis of variance (ANOVA) results for the orthogonal array experimental design are tabulated in Table 3. On the basis of the calculated *F*-values, the iron grade, pH,  $H_2O_2$  addition

#### Table 1

Operating factors and their levels of the  $L_9(3^4)$  orthogonal array experimental design for COD removal and iron consumption

Column	Operating factors	Levels				
		1	2	3		
A	Iron grade	Grade 0000 (Homax <sup>®</sup> )	Brillo®	Grade 3 (Homax <sup>®</sup> )		
В	Initial pH	8.2 (original)	5.0	3.0		
С	$H_2O_2$ addition rate	0	0.5	1.0		
D	Aeration rate (mL air/(min mL) sample)	0	1.3	15.7		

Table 2

Design matrix and the experimental results for the  $L_9(3^4)$  orthogonal array experiments

Experiment	Operating factors and their levels				Mean response	Mean responses		
	A	В	С	D	Overall COD removal (%)	Iron consumption (mg/L)		
1	1	1	1	1	1	0		
2	1	2	2	2	32	4083		
3	1	3	3	3	46	6556		
4	2	1	2	3	40	1698		
5	2	2	3	1	29	1270		
6	2	3	1	2	44	323		
7	3	1	3	2	38	513		
8	3	2	1	3	27	3972		
9	3	3	2	1	25	609		

Column A: iron grade; Column B: initial pH; Column C: H<sub>2</sub>O<sub>2</sub> addition rate  $\eta$ ,  $\eta = [H_2O_2]/2.125 \times COD_0$ ; Column D: aeration rate.

#### Table 3

Analysis of variance (ANOVA) for COD removal efficiencies in the  $L_9(3^4)$  orthogonal array experimental design

Operating factor	Degrees of freedom (d.f.)	Sum of squares (SS)	Mean square (MS)	F ratio
COD removal				
Iron grade	2	0.0570	0.0285	27.0
Initial pH	2	0.0400	0.0200	18.9
$H_2O_2$ addition rate	2	0.0890	0.0445	42.2
Aeration rate	2	0.2550	0.1275	120.8
Error	18	0.0190	0.0011	
Total	26	0.4600		
Iron consumption				
Iron grade	2	$2.9 \times 10^{7}$	$1.5 \times 10^{7}$	25
Initial pH	2	$2.7 \times 10^{7}$	$1.3 \times 10^{7}$	24
$H_2O_2$ addition rate	2	$8.2 \times 10^{7}$	$4.1 \times 10^{7}$	7
Aeration rate	2	$5.7 \times 10^7$	$2.8 \times 10^7$	49
Error	18	$1.0 \times 10^{7}$	$5.8 \times 10^7$	
Total	26	$1.3 \times 10^7$		

Significance level at a 95% confidence interval,  $F(2,18)_{0.05} = 3.0$ ,  $F(2,18)_{0.05} = 2.97$ .

rate, and aeration rate are statistically inferred to have significant influences on COD removal efficiency and iron consumption in treatment of mature leachate. Their order of influence in terms of COD removal was aeration rate >  $H_2O_2$  addition rate > iron grade > initial pH. The corresponding order of influence in terms of iron consumption was aeration rate > iron grade  $\approx$  pH >  $H_2O_2$  addition rate.

Average responses of overall COD removal efficiency and iron consumption for four factors are shown in Fig. 2. Average response can reflect the mean influence of each level of every factor. First, aeration rate was the most significant in terms of COD removal and iron consumption, according to the ANOVA results. However, from Fig. 2, the greatest increase in COD reduction was achieved in going from 0 to 1.3 mL air/(min mL) sample; further increase in COD removal was not significant at the 15.7 mL air/(min mL) sample level. Second, based on ANOVA results, the introduction of H<sub>2</sub>O<sub>2</sub> greatly improved the rate of COD removal. In addition, H<sub>2</sub>O<sub>2</sub> addition rate had the smallest influence on iron corrosion among these factors. Third, the greatest COD reduction and least iron corrosion were observed for the Brillo<sup>®</sup> iron media, a finding that was fortunate though unexplained. The nominal surface area of Fe<sup>0</sup> was not observed to have an obvious relation with COD removal or iron corrosion. Finally, initial pH was the least important factor in terms of COD reduction, and a low initial pH resulted in rapid corrosion, based on ANOVA results. Therefore, in the following experiments, Brillo<sup>®</sup> iron media was selected, and initial pH was not adjusted (8.2).

# 3.2. Effects of aeration rate and $H_2O_2$ dosage

A set of full factorial experiments was carried out to investigate the effects of aeration rate and  $H_2O_2$  addition rate,



Fig. 2. Average responses for COD removal and iron consumption vs. four factors (conditions:  $COD_0 = 1238 \text{ mg/L}$ ): the solid symbols and solid lines represent overall COD removal efficiencies; the hollow symbols and hollow lines represent iron consumption.



Fig. 3. Overall COD removal vs. hydrogen peroxide addition rate (mass concentrated  $H_2O_2/2.125 \text{ COD}_0$ ) at various aeration rates, in the enhanced IMA fixed bed reactor (conditions: initial pH, 8.2; reaction time, 27 h; COD, 1270 mg/L).

along with a no aeration  $(H_2O_2 \text{ alone})$  control group. Aeration rates ranging from 0 to 21 mL air/(min mL) sample were tested, extending the range tested in the Taguchi array. Above the maximum tested aeration rate of 21 mL air/(min mL) sample, leachate foaming was observed to cause loss of sample from the reactor. In addition,  $H_2O_2$  addition rates of 0–4 were tested, also extending the range tested in the Taguchi array tests.

Overall COD removal versus H2O2 addition rates at various aeration rates is shown Fig. 3. Overall COD removal increased with increasing H2O2 addition rate. For H2O2 addition rates >3, the increase in COD removal was marginal. It was also observed that COD removal increased with increasing aeration rate. However, COD removal did not increase significantly above an aeration rate of >14 mL air/(min mL) sample. The maximum COD removal was 50%, significantly higher than was achieved by H2O2 addition alone (7%). Strikingly, 50% removal efficiency achieved in the enhanced IMA process was slightly below 60% of maximum COD removal when the same leachate was treated by Fenton method at pH 3.0 [5]. On the other hand, the ratio of BOD<sub>5</sub>/COD increased with increasing aeration rate in these tests, approximately independent of the H<sub>2</sub>O<sub>2</sub> addition rate, as shown in Fig. 4. The maximum BOD5/COD ratio achieved was 0.17, significantly higher than found in the untreated leachate (0.02) and after treatment with hydrogen peroxide alone (0.08).

### 3.3. Coagulation versus oxidation

Iron sludge, the corrosion products of  $Fe^0$ , was generated over time in the reactor. The previous investigation indicates that the sludge is able to contribute to reduction of organic compounds from landfill leachate through coagulation/flocculation [5]. To estimate the contributions of oxidation and coagulation in the H<sub>2</sub>O<sub>2</sub>-enhanced IMA treatment of leachate, overall COD removal, COD removal by oxidation and by coagulation, were tested, as shown in Fig. 5. In the test, the H<sub>2</sub>O<sub>2</sub> addition rate was fixed at 3, and the aeration rate was fixed at 14 mL air/(min mL)



Fig. 4. BOD<sub>5</sub>/COD vs. hydrogen peroxide addition rate (mass concentration  $H_2O_2/2.125 \times COD_0$ ) at various aeration rates, in the enhanced IMA fixed bed reactor (conditions: initial pH, 8.2; reaction time, 27 h; COD, 1270 mg/L).

sample, both optimal values found previously for overall COD reduction.

As shown in Fig. 5, both oxidation and coagulation contributed to COD reduction. The overall COD removal was near 50%. The ratio of COD removal efficiencies by oxidation to that by coagulation was approximately 4:1. Moreover, oxidation is not attributed primarily to  $H_2O_2$  because the COD removal by  $H_2O_2$  oxidation alone was 3% (Fig. 3), much below 38% achieved by the  $H_2O_2$ -enahnced IMA method (Fig. 5). However, identification of the oxidant species in these complex systems was out of the scope of this study.

Removal by coagulation was attributed to the iron oxyhydroxide-based sludge, produced through iron corrosion and found attached to the fixed fibrous iron and suspended in solution. Although iron corrosion products were not identified in this study, the valence of iron in the sludge was observed visually. During operation, iron sludge in the reactor appeared an orange color, typical of ferric corrosion products. However, upon shaking, the color turned shades of brown. This change may be due



Fig. 5. Overall COD removal, COD oxidation, and COD removal by coagulation in the enhanced IMA fixed bed tests (conditions: initial pH, 8.2; reaction time, 27 h; hydrogen peroxide addition rate, 3; aeration rate, 14 mL air/(min mL) sample; COD, 1270 mg/L).

to a mixing of ferric sludge and ferrous sludge (green). That is, a layer composed of ferrous corrosion products might be formed between the Fe<sup>0</sup> surface and the outer ferric corrosion products where oxidation potential was lower due to inhibition of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> transport from the bulk solution through the oxyhydroxides layer. Moreover, the results of direct COD measurement of the mixed sample (iron sludge and treated leachate) were often greater than the initial COD of leachate, also indicating the existence of ferrous oxyhydroxides that could contribute COD due to oxidation of Fe<sup>II</sup> to Fe<sup>III</sup> and caused overestimation of COD during COD tests. Therefore, the iron sludge produced in H<sub>2</sub>O<sub>2</sub>enhanced IMA treatment may represent a mixture of ferrous and ferric oxyhydroxides.

# 3.4. Effect of stepwise addition of hydrogen peroxide

The effect of the number of  $H_2O_2$  dosing steps on COD removal in the enhanced IMA treatment of leachate was investigated as shown in Fig. 6. Although the nine-step dosing did not improve COD oxidation, overall COD removal was increased by 5%, when compared with single-step dosing for equal total  $H_2O_2$  dosage. This increase was attributed to increased coagulation efficiency, perhaps because stepwise dosing of  $H_2O_2$ decreased, to some extent, auto-decomposition of  $H_2O_2$  due to high localized concentrations, and produced more iron corrosion products for coagulation.

# 3.5. 3D analysis of COD removal versus initial pH and $H_2O_2$ addition rate

Overall COD removal and COD oxidation are shown versus initial pH and  $H_2O_2$  addition rate in Fig. 7(a) and (b), respectively. Low pH significantly enhanced COD removal only at  $H_2O_2$  addition rates of 0–1, consistent with the Taguchi array results. In fact, COD removal efficiencies, both overall and oxidation, depended almost exclusively on the  $H_2O_2$  addition rate, at  $H_2O_2$  addition rates >1. The minor effect of initial pH was apparently because pH starting from an acidic value gradually became neutral due to consumption of H<sup>+</sup> by Fe<sup>0</sup> and selfbuffering effect of aeration. For example, final pH values in the groups with initial pH 3 increased to 6.9 and 7.19, for  $H_2O_2$  addi-



Fig. 6. Effect of the number of dosing steps on overall COD reduction and COD oxidation in enhanced IMA treatment of leachate (conditions: initial pH, 8.2; total reaction time, 9 h; hydrogen peroxide addition rate, 3; aeration rate, 14 mL air/(min mL) sample; COD<sub>0</sub>, 1295 mg/L).



Fig. 7. COD removal in enhanced IMA treatment of leachate (conditions: total reaction time, 9h; dosing step, 9; aeration rate, 14 mL air/(min mL) sample; COD<sub>0</sub>, 1288 mg/L): (a) overall COD removal and (b) COD removal by oxidation.

tion rates of 1 and 9, respectively. Consequently, a part or most of the oxidation actually occurred at near neutral pH, even if the initial pH was 3, such that effect of initial pH became slight. At  $H_2O_2$  addition rates  $\geq$ 3, the increase on overall COD removal was insignificant, again indicating that a  $H_2O_2$  addition rate of 3 was optimal. However, oxidation efficiency had an increasing trend over the tested range of  $H_2O_2$  addition rate, suggesting that the  $H_2O_2$  dosage required to achieve maximum overall COD removal was below that required to achieve maximum COD oxidation.

#### 3.6. Removal of ammonia and electrical conductivity

Removal of ammonia nitrogen (molecular NH<sub>3</sub>-N and ionized NH<sub>4</sub><sup>+</sup>-N) was investigated for the enhanced IMA process at a H<sub>2</sub>O<sub>2</sub> addition rate of 3, as shown in Fig. 8. The removal of ammonia nitrogen in the leachate increased from 0% initially to 83% at 27 h. This result was expected due to maintenance of a weakly basic pH in the reactor, so that a portion of the nitrogen existed as molecular NH<sub>3</sub>-N that was relatively easily stripped from the water through continuous aeration. A chemical reaction occurred when ammonia dissolves in water, as shown in Eq. (1), where ammonia acts as a base, acquiring hydrogen ions from H<sub>2</sub>O to yield ammonium and hydroxide ions.

$$NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$
(1)

The fractions of molecular  $NH_3$ -N can be quantitatively indicated based on the base ionization constant *K*:

$$K = \frac{[\mathrm{NH}_4^+][\mathrm{OH}^-]}{[\mathrm{NH}_3]} = 1.8 \times 10^{-5} \text{ at } 25\,^{\circ}\mathrm{C}$$
(2)

The fraction of molecular NH<sub>3</sub>-N in ammonia nitrogen can be expressed as

$$NH_{3}-N(\%) = \frac{[NH_{3}-N]}{[NH_{4}^{+}-N] + [NH_{3}-N]} = \frac{1}{1 + e^{9.26-pH}}$$
(3)

As shown in Fig. 8, over 27 h the pH increased from 8.05 to 9.07, in which fraction of molecular NH<sub>3</sub>-N accounted for 23–45%. Because nitrogen was slowly removed in the form of NH<sub>3</sub> under air stripping, the equilibration in Eq. (1) was not maintained and the NH<sub>4</sub>+<sub>(aq)</sub> was gradually transformed to NH<sub>3</sub> (Eq. (1)). Consequently, 83% of ammonia nitrogen was removed from the leachate within 27 h. Noticeably, a typical pH of mature landfill leachate is greater than 7.0, implying that the enhanced IMA process can remove ammonia nitrogen without any pH adjustment.

As shown in Fig. 8, removal of electrical conductivity increased to 38% in 9 h when the initial pH was not adjusted, stabilizing thereafter, while corrosion of Fe<sup>0</sup> was continuous with ca. 4000 mg/L Fe<sup>0</sup> consumed over 27 h. Electrical conductivity is often proportional to the TDS in water, and indirectly indicates the content of inorganic ions present in solution because solutions of inorganic compounds are relatively good conductors. Thus, reduction of electrical conductivity indicates removal of inorganic ions. In the enhanced IMA treatment of landfill leachate, two reasons contributed to the reduction of electrical conductivity. First, IMA process did not need external



Fig. 8. Removal efficiencies of ammonia nitrogen and electrical conductivity, pH, and iron consumption vs. time in the enhanced IMA fixed bed reactor (condition: initial NH<sub>3</sub>-N, 300 mg/L; initial electrical conductivity, 8.30 mS/cm).

introduction of acid and salts in the test, different from traditional Fenton treatment that generally requires input of acid (pH adjustment) and ferrous salt. Second, because of precipitation of metal cations by iron sludge produced and coagulation of CaCO<sub>3</sub> and other carbonates after equilibration with atmospheric CO<sub>2</sub>, electrical conductivity was decreased [14]. The quick removal of electrical conductivity within the first 9 h was related to the rapid formation of iron sludge under aeration and addition of H<sub>2</sub>O<sub>2</sub>. But, with the increasing thickness of the corrosion layer, the outer iron corrosion products on the surface might cover the newly generated iron corrosion products below, such that further precipitation was greatly inhibited. As a result, the removal of electrical conductivity was insignificant afterward, though the amount of iron corrosion products continued to increase.

# 4. Conclusion

Based on the laboratory tests, the enhanced IMA process seemed to be a promising process for treatment of mature landfill leachate with high removal efficiency of organic compounds, and simultaneous reduction of ammonia nitrogen and electrical conductivity at a proper pH without pH adjustment. COD removal and iron consumption were influenced by iron grade, initial pH, H<sub>2</sub>O<sub>2</sub> addition rate, and aeration rate. In terms of process design, aeration was found to be essential factor in the reduction of COD in the H2O2-enhanced IMA process. Oxidation and coagulation both contributed to COD reduction. Of note, this process, at a weakly basic initial pH, was shown to achieve 50% COD removal efficiency, slightly below the 60% maximum removal through Fenton treatment (a well-known advanced oxidation process) at acidic pH. In the future experiments, the oxidative species produced in the enhanced IMA process at weakly basic pH is going to be conducted. Furthermore, along with the removal of COD and the enhancement in biodegradability of the organic constituents in the effluent, ammonia nitrogen was substantially reduced due to air bubbling, and electrical conductivity could be significantly removed due to production of iron sludge, when the initial pH was not adjusted (within a weakly basic pH range). Reduction of electrical conductivity indirectly indicated removal of total dissolved solids that may contain some of toxic heavy metals (e.g., As). Thus the enhanced IMA process, in addressing three primary pollutants in landfill leachate, offers a more holistic alternative to technologies designed for removal of one or two of these pollutants.

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