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Treatment of landfill leachate by Fenton process: parametric and kinetic studies

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ABSTRACT

Fenton treatment of leachate of municipal landfill was investigated in this study. Physical and chemical characteristics of the leachate indicated that the waste is alkaline and is characterized by extremely high concentration of organic compounds. Different reaction conditions of Fenton treatment were examined including H_2O_2/chemical oxygen demand (COD) and Fe^{2+}/H_2O_2 ratios in the present work. COD of leachate after Fenton treatment was removed by about 77 and 83% for initial COD 6,250 and 13,300 mgO_2/L, respectively. Such a maximum removal was achieved at pH 3 and using reagent dosages as high as $H_2O_2/COD = 4.4$ and H_2O_2/Fe^{2+}value of 50. Complete oxidation was not achieved even at optimum conditions due to the presence of inhibitors (carbonate) in the leachate wastewater. After removal of high carbonate content, the same removal efficiency could be achieved with lower H_2O_2/COD ratio (i.e. $H_2O_2/COD = 3.3$). A simplified kinetic study for Fenton treatment of leachate wastewater has been performed.

Keywords: Fenton; Landfill leachate; Kinetics; Reaction conditions

1. Introduction

Municipal solid waste (MSW) problems in Egypt have been identified as a top priority issue. MSW comprise of solid waste materials produced in Egyptian homes and businesses as a consequence of everyday activities. The Egyptian average waste generation rate varies from 0.2 kg/person/day in rural areas to 1.0 kg/person/day in large cities. Specific sectors like hotels and tourist resorts may have generation rates as high as 1.5 kg/person/day. Estimates of MSW generation in Egypt are approximately in the range of twenty million tons per year.

MSW releases a liquid waste known as leachate generated from organic matter degradation as well as percolating rainwater entering landfills. The leachate is generated in controlled landfills as well as uncontrolled dumping sites; however, the environmental impact is far greater in uncontrolled dump sites since such sites lack any engineered measures to prevent leachate from contaminating surrounding groundwater and surface water. Thus, landfill leachate can be considered a strongly polluted wastewater [1].

The most important persistent pollutants in landfill leachate that pose a long-term threat to surrounding ground and surface waters are ammonium, xenobiotic organic compounds (aromatic hydrocarbons, chlorinated solvents, pesticides [2], and refractory humic

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substances [3,4]). The concentrations of XOC in landfills are highly variable depending on the extent to which industrial and hazardous substances are included with MSW. The environmental impact of the refractory organic matter is coloration of water due to their dark color, potential role in the formation of disinfection byproducts [5] and increased mobility of heavy metals [6]. Furthermore, toxicity analysis carried out using various test organisms (*Vibrio fisheri, Daphnia similes, Artemiasalina, Brachydaniorerio* etc.) have confirmed the potential dangers of landfill leachates [7–11] and the necessity to treat it so as to meet the standards for discharge in receiving waters.

The removal of organic material from leachate is the usual prerequisite before discharging the leachates, though the satisfactory treatment of landfill leachate is not an easy task due to the high-concentration refractory organics. In general, leachate can be treated by different methods: biological methods (aerobic and/or anaerobic) [12–14] and physicochemical methods: precipitation, oxidation, adsorption, stripping, and reverse osmosis [15–17]. Biological technologies for landfill leachate treatment have been shown to be economic and effective methods to degrade readily biodegradable organic matter such as volatile fatty acids. Many oxidation technologies have been developed to facilitate the degradation of nonbiodegradable organic compounds present in old leachate. All these technologies have one common characteristic in that the removal processes are based on the creation of very reactive oxidizing free radicals, especially the OH radical ($^{\bullet}OH$).

Fenton's reaction is one of advanced oxidation process (AOPs) that can be described as the generation of $^{\bullet}OH$ radicals through catalytic decomposition of hydrogen peroxide (H_2O_2), carried out by a transition metal such as ferrous iron (Fe^{2+}) (Eq. 1):

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^{-} + Fe^{3+} \tag{1}$$

Fenton process has been studied extensively in recent years [18–20] and it has been confirmed as a highly effective alternative for degrading recalcitrant organic matter in a variety of wastewaters, including landfill leachate. For instance, 60–70% chemical oxygen demand (COD) removal in leachate wastewater was achieved by Fenton process under the best tuned conditions [21–23]. Moreover, Kang and Hwang [24] achieved a constant 70% maximum COD removal at different iron dosages, differentiating between oxidation and coagulation contributions to COD removal (45–55% COD removal was attributed to the oxidation process efficiency, while the rest 15–25% was removed by coagulation). Combined AOPs technologies were also used for the degradation of landfill leachate. Ozone and mixture of hydrogen peroxide/ozone were used for detoxification of refractory organic pollutants ion leachate [25,26]. Abu Amr and Abdul Aziz used combined ozone and Fenton oxidation to achieve 65% removal of COD of pretreated leachate (i.e. initial COD = 2,180 mg O_2/L) [27].

This study focuses on the optimization of Fenton treatment of landfill leachate of different COD strengths with the aim of making technically and economically feasible this method at practical scale. Kinetics of Fenton reaction has also been studied.

2. Experimental

2.1. Materials

Leachate samples were collected from a municipal landfill in Borg El Arab town located 60 km away from the city of Alexandria, Egypt. Samples were preserved in refrigerator at 4°C and transferred to the laboratory for analysis. The analysis covered conventional parameters as well as organic pollutants.

Reagent grade ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) as a source of Fe^{2+} catalyst in Fenton process, sulfuric acid, and sodium hydroxide were purchased from Merck Company, Germany. Hydrogen peroxide solution (30%, w/w) in stable form was provided by Fluka Company, Germany. All reagents were used without further purification.

2.2. Procedure of Fenton process

Bench-scale batch experiments were carried out at room temperature to determine optimum operating conditions of the reaction. One-liter cylindrical glass vessel was used for this purpose. The predetermined ferrous sulfate dose was added to 500 ml leachate sample. The mixture was acidified using sulfuric acid to enhance the oxidation [28,29]. This was followed by the addition of hydrogen peroxide under vigorous stirring to start Fenton reaction. The reaction time lasted for 4 h, during which the treated samples were collected each half an hour for analysis. The pH of the wastewater samples were raised up to nine by NaOH for two reasons; precipitation of dissolved Fe^{3+} and degradation of residual H_2O_2. To ensure complete removal of residual H_2O_2, samples were heated to 60°C for 30 min. This was followed by filtration using 0.45 μm membrane to separate the precipitated ferric hydroxide. These experiments were repeated using different ratios of H_2O_2/COD, H_2O_2/Fe^{2+} and pH values.

2.3. Analytical methods

COD and other physicochemical parameters of the samples were measured according to APHA [30]. Total organic carbon was measured using Phoenix TOC Analyzer (USA) equipped with boat sampler183. Polyaromatic hydrocarbons (PAHs), phenols, organochlorine pesticides and polychlorinated biphenyls (OCPs and PCBs) analyses were carried out according to USA EPA methods number 8100, 604 and 8081B, respectively.

3. Results and discussion

3.1. Characteristics of leachate wastewater

Physical and chemical characteristics of the leachate samples are summarized in Table 1. It was indicated that the waste is alkaline and has a strong black brownish color that is considered undesirable property. Another negative impact of wastewater is extremely high content of ammonia concentration (5,180 mg N/l) and organic compounds, which is reflected by the high mean values of COD and total organic content (TOC) (13,650 and 6,110 mg/l, respectively). The COD/biochemical oxygen demand (BOD) ratio ranges from 0.44 to 0.46 with an average value of 0.45, compared with a ratio of 0.66 for domestic wastewater.

Table 1
Characterization of leachate of Borg Al-Arab site

Parameter	Unit	Average
Physical–chemical analyses		
pH	–	8.5
Total COD	mgO_2/L	13,650
Soluble COD	mgO_2/L	10809.5
BOD5	mgO_2/L	6,110
BOD/COD	–	0.45
TOC	mgC/L	5,868
TSS (105°C)	mg/L	738
VSS (550°C)	mg/L	398.5
TKN	mgN/L	5,727
NH4-N	mgN/L	4,830
Total-P	mgP/L	77
Chloride	mg/L	4,325
Organic analyses		
PAHs	μg/L	4024.26
OCPs	ng/L	3202.513
PCBs	μg/L	ND
Phenolic	μg/L	1376.32

Results of the analyses of organic compounds in leachate showed in Table 1 and the average of PAHs concentration in the leachate was 4,024.26 μg/L. Nine compounds of PAHs were detected (data not shown). The most abundant individual compounds of PAHs were naphthalene (1,583.69 μg/L), chrysene (675.34 μg/L), phenanthrene (401.65 μg/L) and flourene (275.79 μg/L), while naphthalene derivatives were not detected. Also, three-membered aromatic hydrocarbons were detected; Fluoranthene (174.78 μg/L), Pyrene (164.9 μg/L) and Benzo (a) anthrancene (200.72 μg/L). Also, the average concentration of total chlorinated pesticides was 3,202.51 ng/L. Only three chlorinated pesticides were detected namely; β-HCH, δ-HCH and Heptachlor (606.82, 2,192.28 and 807.96 ng/L, respectively). The most abundant pesticide was Heptachlor. Other pesticides were less than the detection limit. On the other hand, polychlorinated biphenyls (PCBs) were not detected. Moreover, the average concentration of phenols in leachate was 1,376.32 μg/L. Only three phenolic compounds were detected namely; phenol (18.25 μg/L), 2-nitrophenol (940.65 μg/L) and 2,3-dimethylphenol (317.4 μg/L). These detected compounds are represented persistent organic pollutants (POPs).

3.2. Optimization of Fenton process

3.2.1. Effect of hydrogen peroxide concentration

Hydrogen peroxide is the key factor in Fenton process. The concentration of hydrogen peroxide used in Fenton process relies mainly on initial COD value according to the stoichiometric ratio between COD and hydrogen peroxide:

$$1 \text{ g COD} = 1 \text{ g } O_2 = 0.03125 \text{ mol } O_2$$

$$2H_2O_2 \rightarrow O_2 + H_2O \qquad (2)$$

Therefore 0.03125 mole O_2 needs 0.0625 mol $H_2O_2 = 2.125$ g H_2O_2. However, this ratio is not valid for all types of wastewater especially that contains inorganic materials in addition to organic compounds. In this study different H_2O_2/COD ratios, ranging from 1.1 to 5.5, were investigated in order to determine the optimum ratio for the treatment of two different initial COD strength wastewaters. pH was kept at 3 and H_2O_2/Fe^{2+} molar ration = 50. Aliquot of the sample was taken regularly from the reaction in order to determine the residual COD, TOC.

Figs. 1 and 2 illustrate the effect of hydrogen peroxide concentration on the percent removal of COD and TOC, respectively. COD% and TOC% removal

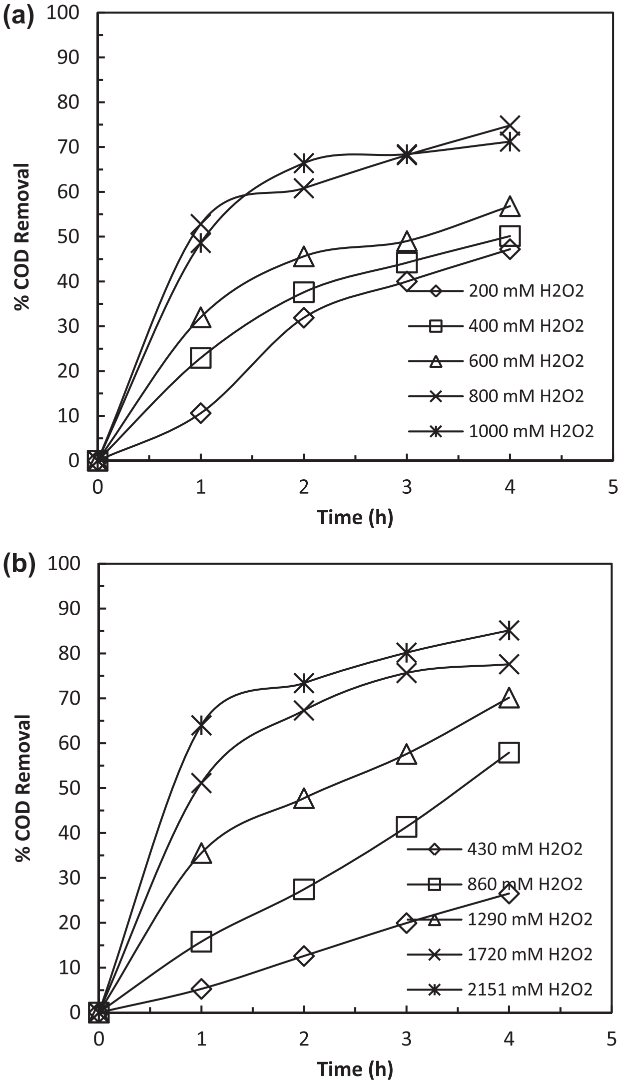

Fig. 1. Effect of H_2O_2 concentration on %COD removal; (a) $COD_i = 6{,}250\,mgO_2/L$ and (b) $COD_i = 13{,}300\,mgO_2/L$; pH = 3 and $H_2O_2/Fe^{2+} = 50$.

were increased with the increasing hydrogen peroxide concentration. The increase in H_2O_2 concentration led to an increase in the reaction rate as more $^{\bullet}OH$ radicals were generated [31]. Maximum COD% removal was found to be 74.8 and 77.59%, while maximum TOC% removal was 76.93 and 84.93% for $COD_i = 6{,}250\,mgO_2/L$ and $COD_i = 13{,}300\,mgO_2/L$, respectively. The maximum removal was achieved at $H_2O_2/COD = 5.5$; however, the difference in removal percent in case of $H_2O_2/COD = 4.4$ and $H_2O_2/COD = 5.5$ was minute. So that $H_2O_2/COD = 4.4$ was assumed to be the optimum ratio. Comparing removal percentages in case of low and high COD strength illustrates that higher initial COD strength is easier for degradation using Fenton process.

3.2.2. *Effect of Fe^{2+} concentration*

The ratios of hydrogen peroxide to ferrous iron (H_2O_2/Fe^{2+}) and of organic materials to ferrous iron (RH/Fe^{2+}) are very important operational parameters of the Fenton process. In order to investigate the optimum H_2O_2/Fe^{2+} molar ratio, five different H_2O_2/Fe^{2+} molar ratios were tested with two different COD strengths (6,250 and 13,300 mg/L). The hydrogen peroxide dosage was held constant (800 and 1,720 mM for 6,250 and 13,300 mgO_2/L initial COD, respectively) while Fe^{2+} dosage changed to yield a H_2O_2/Fe^{2+} molar ratio ranging from 25 to 150. pH was kept constant at 3 ± 0.1. At definite interval times, an aliquot of the sample was taken from the reaction in order to measure residual COD and TOC.

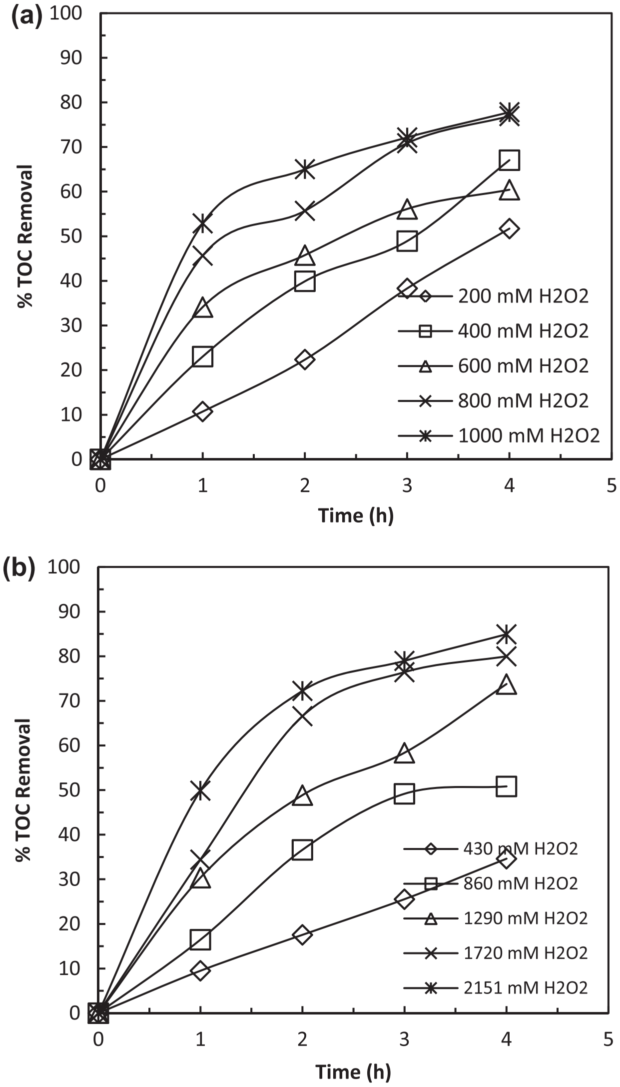

Fig. 2. Effect of H_2O_2 concentration on %TOC removal; (a) $COD_i = 6{,}250\,mgO_2/L$ and (b) $COD_i = 13{,}300\,mgO_2/L$; pH = 3 and $H_2O_2/Fe^{2+} = 50$.

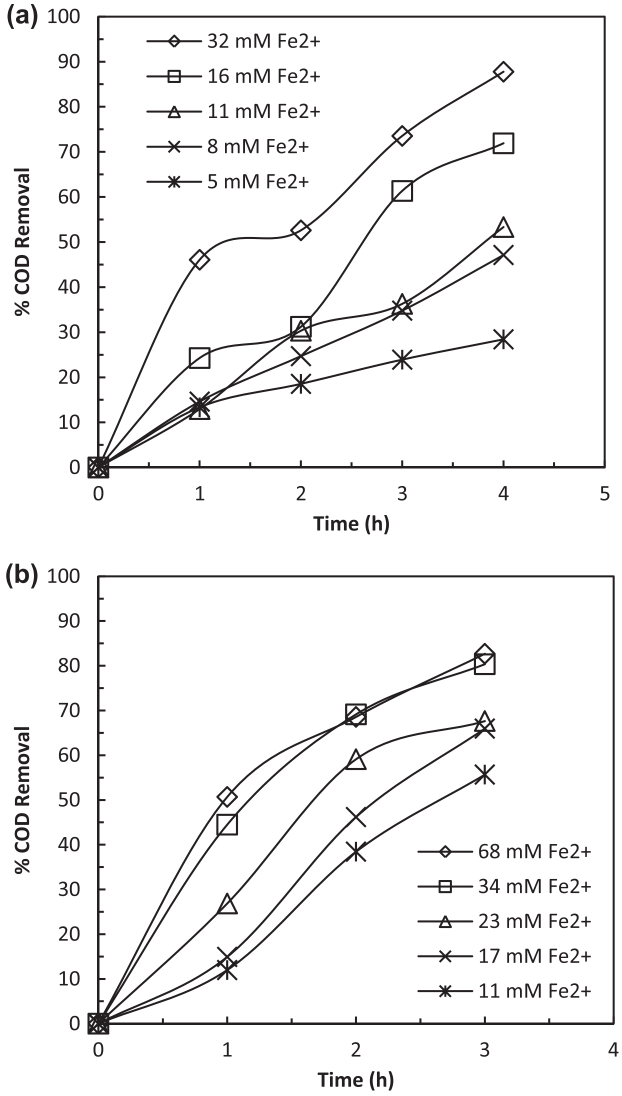

Fig. 3. Effect of Fe^{2+} concentration on %COD removal; (a) $COD_i = 6{,}250\,mgO_2/L$ and (b) $COD_i = 13{,}300\,mgO_2/L$; pH = 3 and $H_2O_2/COD = 4.4$.

The changes of COD and TOC removal efficiencies are shown in Figs. 3 and 4. These increased with the reduction of H_2O_2/Fe^{2+} molar ratio by 25. For 6,250 mgO_2/L COD_i, COD% removal was only 30% at the molar ratio of 150 but increased to 87.77% at the molar ratio of 25, while the improvement of COD removal was from 55.68% at molar ratio 150 to 82.69% at the molar ratio of 25 in case of 13,300 mgO_2/L COD. This improved COD removal might be caused by the change of the reaction condition between organic materials and Fenton's reagent [32]. TOC% removal exhibited the same enhancement when H_2O_2/Fe^{2+} reduced from 150 to 25. Observed COD removal percentage is slightly higher than that stated by Hermosilla et al. [33] but is still in the range of reported COD removal efficiencies using Fenton process from 45 to 85% [27].

The optimum H_2O_2/Fe^{2+} molar ratio was considered to be 50, where there is no significant removal improvement when the ratio of H_2O_2/Fe^{2+} was increased to 150. This result might be attributed to the scavenging effect of peroxide on the $^{\bullet}OH$ radicals, which presumably became stronger as the ratio H_2O_2/Fe^{2+} increased. Another explanation can be the formation of hydroperoxyl radicals ($HO_2^{\bullet}$), which are less reactive in attacking the recalcitrant compounds in the liquid phase [34]. There are a lot of compounds in the leachate that scavenge these radicals, not allowing a significant oxidation to proceed such as carbonate, chlorides, and sulfate [35]. Furthermore,

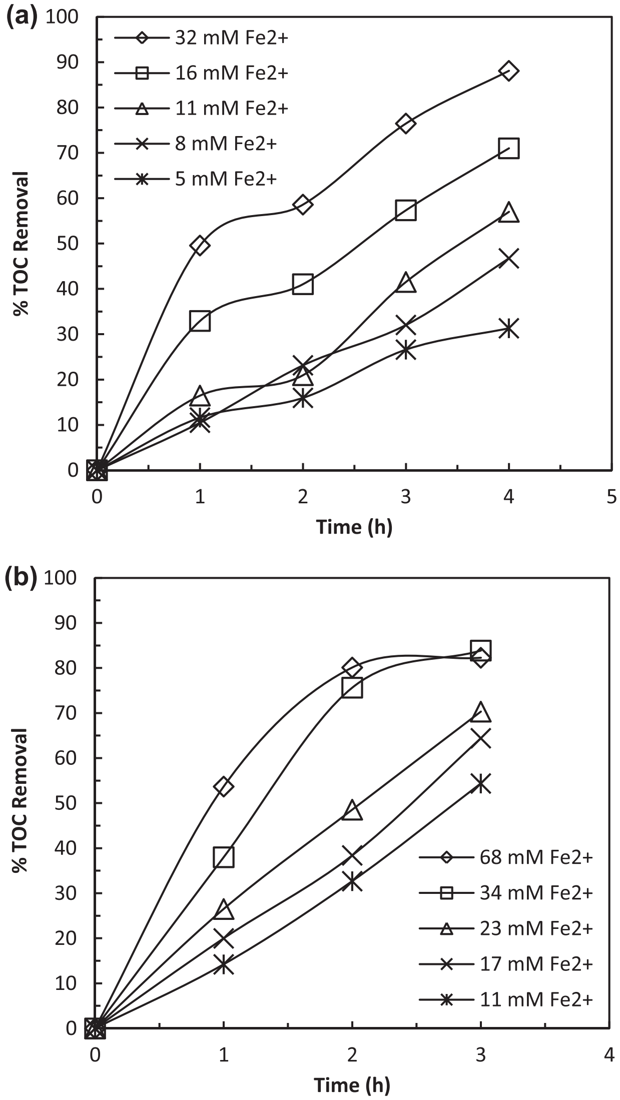

Fig. 4. Effect of Fe^{2+} concentration on %TOC removal; (a) $COD_i = 6{,}250\,mgO_2/L$ and (b) $COD_i = 13{,}300\,mgO_2/L$; pH = 3 and $H_2O_2/COD = 4.4$.

the lower molar ratio is more favorable because lower Fe^{2+} is used which should reflect positively on the treatment cost due to lower consumption of chemicals and lower sludge production (ferric hydroxide) after completion of Fenton process [36]. Based on the results obtained, optimum reaction conditions for the leachate wastewater with different initial concentrations are $COD:H_2O_2 = 1:4.4$ and $Fe^{2+}:H_2O_2 = 1:50$.

From the obtained results, it can be concluded that even at optimum conditions, complete oxidation was not possible. This might be due to the presence of inhibitors in the leachate wastewater such as: high alkalinity, chlorides, sulfates, etc. The leachate wastewater was found to contain 17,400 $mgCaCO_3/L$ total alkalinity, 2,000 mg/L carbonate, 15,400 mg/L bicarbonate and 4,325 mg/L chloride which explains the violent effervescence during pH adjustment ($pH = 3$) due to high carbonate content.

Inorganic carbons can be easily removed by controlling the pH to the acidic condition then purge the sample with air to get rid of formed carbon dioxide. About 500 ml of leachate wastewater was adjusted to pH 3 then aerated for long time. About 95% of alkalinity could be removed after only 10 min of aeration. This proves that most of inorganic carbon has been converted to carbon dioxide and evolved from wastewater during aeration.

3.3. Optimization of Fenton reaction for aerated leachate wastewater

3.3.1. Effect of H_2O_2 concentration

Wastewater of 6,725 mgO_2/L initial COD was used to optimize Fenton reaction for aerated wastewater. Different H_2O_2 concentrations have been investigated ranging from 218—870 mM which corresponds to H_2O_2/COD weight ratio from 1.1 to 4.4. There was a noticeable improvement in Fenton process after removal of inorganic carbon. For instance, 80.74% of COD and 84.87% of TOC removals were achieved with only 653 mM H_2O_2 (H_2O_2/COD weight ratio = 3.3) in case of aerated wastewater. In contrast, only 77.37% of COD and 75.55% of TOC removals were obtained when H_2O_2/COD weight ratio = 4.4 in case of nonaerated wastewater. This about 10% improvement could be attributed to the removal of inorganic carbon (as carbonate and bicarbonate) which is well-known radical scavenger [35].

3.3.2. Effect of Fe^{2+} concentration

In order to investigate the effect of ferrous ion concentration on Fenton treatment of aerated wastewater of $COD_i = 6{,}725$ mgO_2/L, H_2O_2 concentration was kept constant at 652.72 mM (H_2O_2/COD weight ratio = 3.3) while ferrous ion concentration has been changed from 26.11 to 6.53 mM which corresponds to Fe^{2+}/H_2O_2 molar ratio 25 and 100, respectively. Optimum ferrous ion concentration was decided to be 13.05 mM (Fe^{2+}/H_2O_2 molar ratio = 50) as at this concentration maximum removal rate of TOC (81%) and COD (80.74%) were achieved. The optimum conditions of leachate wastewater after aeration was identified to be $COD:H_2O_2 = 1:3.3$ (652.72 mM H_2O_2) and $Fe^{2+}:H_2O_2 = 1:50$ (13.05 mM Fe^{2+}).

From previous results, it is clear that Fenton reaction is still not able to degrade all organic compounds present in wastewater even when using optimum reaction conditions and after aeration of wastewater. This might be due to the presence of radical scavenger other than carbonate and bicarbonate in wastewater. However, the obtained results in this study are promising and exceed the other results reported in the literature [21–23].

3.4. Kinetic study of Fenton reaction used for the treatment of leachate wastewater

It is very complicated to perform a detailed kinetic study for Fenton treatment of leachate wastewater due to the heterogeneous composition of the leachate wastewater and, additionally, to the complexity of chemical compounds formed as intermediates in the Fenton reagent oxidation. In this study, an approximated kinetic study according to some parameter that represents the overall organic matter; in this case, the TOC (to avoid any interference in COD measurements stemmed from inorganic precursors in wastewater) was carried out. Only sample of 13,300 mgO_2/L COD was chosen to apply the kinetic study. In general, Fenton reaction could be described by the following reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \tag{3}$$

Then hydroxyl radicals attack the organic pollutants in wastewater represented by TOC as follows:

$$HO^{\bullet} + TOC \rightarrow CO_2 + H_2O \tag{4}$$

Yielding an overall reaction of:

$$Fe^{2+} + H_2O_2 + COD \rightarrow Fe^{3+} + HO^{-} + \text{Decomposition product}$$

Accordingly, the equation that describes the rate of this reaction is:

$$-\frac{d\mathrm{COD}}{dt} = k\,C^{l}_{\mathrm{COD}} C^{m}_{\mathrm{Fe}^{2+}} C^{n}_{\mathrm{H_2O_2}} = k_{\mathrm{app}} C^{l}_{\mathrm{TOC}} \tag{5}$$

$$k_{\mathrm{app}} = k\,C^{m}_{\mathrm{Fe}^{2+}} C^{n}_{\mathrm{H_2O_2}} \tag{6}$$

where k = actual rate constant, k_{app} = apparent rate constant, C = concentration and l, m and n are the order of reaction in COD, Fe^{2+} and H_2O_2, respectively. Under all studied H_2O_2 concentrations (430–2,151 mM H_2O_2), the order of reaction obeyed pseudo-first-order kinetics in TOC concentration. The plot of k_{app} against H_2O_2 concentration in logarithmic scale resulted in a straight line (Fig. 5), from which order of reaction in H_2O_2 concentration could be deduced using the formula:

$$\ln k_{\mathrm{app}} = \ln k_1 + n \ln [\mathrm{H_2O_2}] \tag{7}$$

It was found that $n = 1$ for $\mathrm{COD}_i = 13{,}300\,\mathrm{mgO_2/L}$, which reveals that the rate of reaction depends on H_2O_2 concentration as well as wastewater load.

For the determination of reaction order in Fe^{2+} concentration, the first-order kinetics of COD degradation by Fenton reaction using different Fe^{2+} concentration (11–68 mM Fe^{2+}) was plotted and apparent rate constant was calculated. At constant H_2O_2 concentration, the apparent rate constant is proportional to Fe^{2+} concentration according to the following equation:

$$k_{\mathrm{app}} \propto C^{m}_{\mathrm{Fe}^{2+}} \rightarrow k_{\mathrm{app}} = k_2 C^{m}_{\mathrm{Fe}^{2+}} \tag{8}$$

According to Fig. 6, order of reaction in Fe^{2+} equals 0.7 for $\mathrm{COD}_i = 13{,}300\,\mathrm{mgO_2/L}$.

The overall reaction rate equation can be summarized in:

$$-\frac{d\mathrm{COD}}{dt} = k\,C_{\mathrm{COD}}\,C^{0.7}_{\mathrm{Fe}^{2+}}\,C^{1}_{\mathrm{H_2O_2}} \tag{9}$$

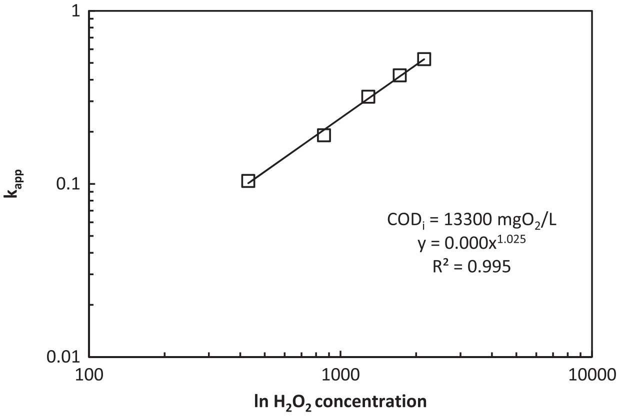

Fig. 5. Change in k_{app} as a function of H_2O_2 concentration.

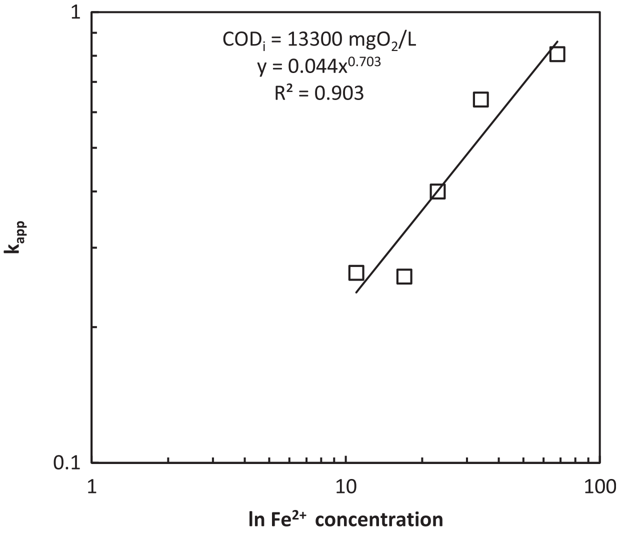

Fig. 6. Change in k_{app} with Fe^{2+} concentration.

For $\mathrm{COD}_i = 13{,}300\ \mathrm{mgO_2/L}$

4. Conclusion

Fenton was effectively used to reduce concentrations of organic contaminants and color of landfill leachate wastewater. The maximum amount of COD that could be removed by the Fenton's treatment was about 77 and 83% of the initial value of initial COD values 6,250 and 13,300 $\mathrm{mgO_2/l}$, respectively. Such a maximum removal was achieved at pH 3 and using reagent dosages as high as 800 mM/l of H_2O_2 and 16 mM/l of Fe^{2+} for the initial COD value of 6,250 $\mathrm{mgO_2/l}$. These values corresponding the COD: H_2O_2 = 1:4.4 and H_2O/Fe^{2+} value of 50:1. Aeration leachate wastewater was found to assess in the improvement of Fenton reaction as a result of taking away of radical scavenger, that is, carbonate, by aeration. Kinetic study proved that order of reaction in Fe^{2+} and H_2O_2 were 0.7 and 1, respectively.

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