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ORIGINAL ARTICLE

Biodegradability Enhancement of Mature Landfill Leachate Using Fenton Process under Different COD Loading Factors

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Abstract The Fenton process is evaluated as a treatment method to reduce the total organic carbon (TOC) and increase biodegradability of the organic substrate in a mature landfill leachate. Biodegradability was quantified in terms of the ratios between biochemical oxygen demand after 5 days (BOD_5) to chemical oxygen demand (COD) (after different Fenton reaction times), and BOD_5 (after different Fenton reaction times) to initial BOD_5 (original leachate sample), termed as $BOD_{5,0}$, respectively. An increased TOC removal and improved BOD_5/COD ratios were observed following the pH sequence of $3.5 > 6.0 > 2.0$. The maximum TOC removal of 61 % and the highest BOD_5/COD ratio from 0.11 to 0.37 were observed at pH 3.5. To quantify biodegradability enhancement at different COD loading factors (L_{COD}) by the Fenton process, the H_2O_2/Fe^{2+} ratio was fixed at 1.8 (*w*/*w*) and L_{COD} ranged from 0.22 to 1.19. Experimental results showed that higher TOC removal and biodegradability enhancement were obtained at lower L_{COD}. Quantitatively, two linear regression equations between L_{COD} and biodegradability (in terms of BOD_5/COD and $BOD_5/BOD_{5,0}$) were established, as: $BOD_5/COD = 0.57–0.38\ L_{COD}$ and $BOD_5/BOD_{5,0} = 1.40–0.40\ L_{COD}$ with correlation coefficients (R^2) of 0.87 and 0.51, respectively. The experimental work described here, demonstrated

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that the Fenton process can be used as an effective pre-treatment strategy to increase leachate biodegradability within a short reaction time from 1 to 5 min.

Keywords Leachate biodegradability enhancement · Fenton process · COD loading · BOD_5/COD ratio · $BOD_5/BOD_{5,0}$ ratio

1 Introduction

Landfill leachate typically contains high concentrations of dissolved organic matter (OM) and inorganic compounds such as ammonia. Therefore, it may impose a considerable risk of impairing the water quality of the receiving aquatic systems if leachate was discharged to either surface or groundwater without any treatment (EPA 1988). To prevent contamination of aquatic systems, conventional biological wastewater treatment technologies are effective when organic compounds in wastewater are biodegradable. However, biodegradability of leachate varies greatly as function of waste composition and age. Typically, biodegradable OM is dominant in leachate composition during the first few years of landfill operation. As the landfill ages, the biodegradable portion is depleted and the organic load is enriched in recalcitrant organic compounds, such as humic and fulvic OM with heavy metals and toxic organic pollutants (de Morais and Zamora 2005; Batarseh et al. 2007; Naumczysky et al. 2012). Advanced oxidation processes (AOPs) are among the alternative treatment technologies that have been proposed for effective treatment of leachate at this stage (Wang et al. 2003; Deng and Englehardt 2006). Among the AOPs, great attention has been given to Fenton process (Zhang et al. 2005; Umar et al. 2010; Cortez et al. 2011). During Fenton oxidation, hydroxyl radical is generated in a homogeneous medium by mixing of hydrogen peroxide with ferrous iron at room temperature in the dark, as follows (Eq. 1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + HO^- \qquad k = 76\ M^{-1}.s^{-1} \tag{1}$$

The theoretical amount of H_2O_2 required for oxidation on a mass-basis is equal to 2.125 times the mass of molecular oxygen (Eq. 2); that is, 2.125 times the initial chemical oxygen demand (COD) (Gernjak et al. 2003).

$$2H_2O_2 \rightarrow 2\ H_2O + O_2 \tag{2}$$

At a much slower process, the ferric ions generated in Eq. (2) will be reduced to ferrous ions by H_2O_2:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+\ k = 10^{-3}-10^{-2}M^{-1}.s^{-1} \tag{3}$$

The Fenton process offers many advantages. For example, chemical reagents used are abundant, inexpensive and environmentally benign. In addition, the Fenton process is a homogeneous catalytic process in nature without mass transfer limitation. Fenton reaction requires low pH values in the range from 2.5 to 3.5 (Pignatello 1992; Nogueira and Guimarães 2000). As a result, two steps are necessary for effective oxidation of organic pollutants: (1) before the Fenton process, the pH has to be adjusted to 2.5–3.5; and (2) after the Fenton process, lime has to be added to raise pH to the neutral value so that the treated waters could be discharged to sewers or surface waters.

Since the rate constant of Eq. (3) is three orders of magnitude smaller than that of Eq. (1), ferrous ions are usually regenerated slowly through Eq. (3). Therefore, a high initial amount of

Fe^{2+} is necessary to obtain high degradation efficiency. As a result, a large amount of ferric hydroxide sludge will be generated. To determine the optimal dose of H_2O_2 and Fe^{2+}, laboratory experimental work is usually carried out to optimize chemical reagents for each specific leachate. In this paper, the COD loading factor (L_{COD}) is used as a key variable during the quantification of biodegradability enhancement of leachate by Fenton process. Since the H_2O_2 demand is only determined by the soluble COD of leachate during Fenton oxidation at pH 3.5 (Singh and Tang 2013), quantitative correlations between the ratios of BOD_5/COD or $BOD_5/BOD_{5,0}$ with L_{COD} could be considered as universally applicable for biodegradability enhancement of mature leachate by the Fenton process.

The Fenton process was investigated as an effective and inexpensive pre-treatment for biodegradability enhancement of leachate. Many experimental works have showed that the toxic and recalcitrant compounds could be degraded by the Fenton process to low weight organic compounds, which generally show higher biodegradability (Lopez et al. 2004; Goi et al. 2010; Gotvajn et al. 2011; Nurisepehr et al. 2012; Vilar et al. 2013). Although many applications of the Fenton processes to improve landfill leachate biodegradability have been reported (e.g., Goi et al. 2010; Gotvajn et al. 2011; Nurisepehr et al. 2012; Vilar et al. 2013; Singh et al. 2013), these previous studies did not report the role of pH on biodegradability when the Fenton process was evaluated as an alternative to the pre-treatment of mature landfill leachate to improve the biodegradability. In addition, no quantitative relationship between the biodegradability enhancement and the mass ratio of COD present in leachate to available oxygen in H_2O_2, referred to as COD loading factor (L_{COD}), was ever reported. Therefore, the objectives of this study were to evaluate the biodegradability enhancement in terms of either BOD_5/COD or $BOD_5/BOD_{5,0}$ ratios under different L_{COD} values. The BOD_5/COD ratio reflects biodegradability enhancement of non-biodegradable OM to biodegradable OM in leachate, while the $BOD_5/BOD_{5,0}$ ratio reflects biodegradability enhancement after Fenton process compared to its $BOD_{5,0}$ before Fenton treatment. The quantitative relationships between BOD_5/COD or $BOD_5/BOD_{5,0}$ with L_{COD} should be valid for biodegradability enhancement of mature leachate by Fenton process due to the dimensionless nature of the correlation equations to be established in this study. As a result, it may be used to estimate the amount of oxidant, H_2O_2, required to achieve a specific biodegradability improvement in terms of either BOD_5/COD or $BOD_5/BOD_{5,0}$.

2 Materials and Methods

2.1 Sampling

Leachate samples were collected from a lined municipal solid waste landfill located in north Palm Beach County, Florida, with a waste age greater than 20 years. The work presented here refers to the analysis of two distinct leachate samples, labeled as leachates A and B. Leachate A was a mixed leachate collected from all the cells of the landfill. It includes drainage from cells containing municipal solid waste (MSW) and others containing ash from a waste to energy plant. Leachate B was collected from a cell only containing MSW. Samples were placed in a 20-L Nalgene container and stored in a refrigerator at 4 °C in the dark until used in the experiments.

2.2 Reagents

Ultrapure water, with an electrical resistivity higher than 16 $Mohms.cm^{-1}$ and total organic carbon (TOC) lower than 75 $\mu g.\ L^{-1}$, was used in the experiments. Technical grade

$FeSO_4.7H_2O$, NaOH and H_2SO_4 were purchased from Fisher Scientific, while H_2O_2 (35 % *w*/*w*) was purchased from Acros Organics.

2.3 Fenton Experiments

Batch experiments were conducted using 1 L of raw leachate, and/or diluted leachate with ultrapure water, in a 2 L jar test apparatus (Phipps and Bird, Richmond, VA) set at a rotation speed of 100 rpm. Before starting the experiments, the leachate samples were brought to room temperature at about 23 °C. Then, the leachate samples were shaken for re-suspension of settled solids and diluted to produce solutions with volumetric ratios ranging from 10 to 83 % (*v*/*v*). The pH range (2.0–6.0) and H_2O_2/Fe^{2+} ratio (1.8 *w*/*w*) used in the experiments were chosen according to the statistical analysis of optimal Fenton leachate treatment conditions (Singh and Tang 2013). The previously published literature had determined the H_2O_2 dose by conducting multiple experiments at a variable number of doses using trial or using different ratios of H_2O_2 and COD (Lopez et al. 2004; Goi et al. 2010). In this study, we hypothesized that the selection of Fenton reagent dose should be decided depending upon the amount of available O_2 in the form of $^{\bullet}OH$ that is present for oxidation of organic matter, given by the initial COD value. Therefore, the oxidant (H_2O_2) dose was based on the ratio of initial COD of leachate landfill and O_2 supplied by H_2O_2, which is also termed as L_{COD} (Eq. 4):

$$L_{COD} = \left(\frac{MassCOD_{initial}\left(mg.L^{-1}\right)}{O_{2available}\left(mg.L^{-1}\right)}\right) = \left(\frac{MassCOD_{initial}\left(mg.L^{-1}\right)}{0.47x[H_2O_2]\left(mg.L^{-1}\right)}\right) \quad (4)$$

where ‘available O_2’ is the theoretical amount of reactive O_2 equivalent to the added H_2O_2. Theoretically, 1 mol of H_2O_2 (34 g H_2O_2) has 0.50 mol of available O_2 (16 g O_2) for oxidation, according to Eq. (5):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (5)$$

In the first part of this study, experiments were carried out to evaluate the effect of initial pH of 2.0, 3.5 and 6.0 on TOC removal and biodegradability enhancement, in terms of BOD_5/COD or $BOD_5/BOD_{5,0}$ ratios at L_{COD} 0.61 and H_2O_2/Fe^{2+} 1.8 (*w*/*w*). In these essays (experiments 1–3; Table 1), the raw leachate A was diluted by 50 % (*v*/*v*), generating different organic load solutions (TOC=85±11 mg. L^{-1}; COD=515±68 mg. L^{-1}; BOD_5=30±13 mg. L^{-1}). Each experiment was started by stirring the leachate at 100 rpm while pH was adjusted to a desired value using 10 mol. L^{-1} H_2SO_4 and/or 1 mol. L^{-1}NaOH. The desired amount of $FeSO_4.7H_2O$ crystals were weighed and dissolved separately in a beaker using leachate from the same jar-test beaker. The dissolved $FeSO_4.7H_2O$ was then added to the stirred leachate. After 1 min, the desired amount of H_2O_2 was added in a single step. To monitor the process, 20 mL sample aliquots were taken from the batch reactor after 0.5, 1 and 5 min, sequentially, followed by coagulation/flocculation/decantation. The pH was raised to 10 by using 10 mol. L^{-1} NaOH. After this, the supernatant was collected and kept in the dark at 4 °C until analyzed for TOC and BOD_5. In addition, pH values greater than 10 also contributed to quench the oxidation reaction by terminating the production of $^{\bullet}OH$ radicals, since the excess of H_2O_2 is released as O_2 (Papadopoulos et al. 2007). This step is very important to prevent any further reaction, as well as eliminate the H_2O_2 interference on COD or BOD_5 analysis (Wu and Englehardt 2012).

In the second set of essays (experiments 2 and 4; Table 1), an initial pH of 3.5 and H_2O_2/Fe^{2+} 1.8 (*w*/*w*) were used. Raw leachate A was diluted between 16 and 84 % (*v*/*v*) generating different organic loadings ([TOC]=109±39 mg L^{-1}; [COD]=665±246 mg L^{-1}; [BOD_5]=52±

Table 1 Experimental conditions used in Fenton leachate treatment, fixing the H_2O_2/Fe^{2+} ratio at 1.8 (*w*/*w*)

Experimental	Initial experimental conditions							
	TOC (mg. L^{-1})	COD (mg. L^{-1})	BOD_5 (mg. L^{-1})	pH	L_{COD}	H_2O_2 (mg. L^{-1})	Fe^{2+} (mg. L^{-1})	Sampling time (min)
1	91	555	18	2.0	0.61	1,944	1,080	0, 0.5, 1 and 5
2	69	419	47	3.5	0.61	1,458	810	0, 0.5, 1 and 5
3	94	571	24	6.0	0.62	1,944	1,080	0, 0.5, 1 and 5
4	148	912	57	3.5	1.00	1,944	1,080	0, 0.5, 1 and 5
5	249	1,543	30	3.5	1.12	2,916	1,620	5
6	20	111	27	3.5	0.34	691	384	5
7	30	171	36	3.5	0.53	691	384	5
8	73	442	50	3.5	1.02	920	511	5
9	124	763	72	3.5	1.18	1,381	767	5
10	24	134	36	3.5	1.14	250	139	5
11	25	140	30	3.5	1.19	250	139	5
12	42	247	55	3.5	0.22	2,324	1,291	5
13	41	239	42	3.5	0.66	774	430	5
14	49	289	39	3.5	1.06	581	323	5
15	187	1,155	124	3.5	1.06	2,324	1,291	5
16	76	460	95	3.5	0.21	4,648	2,582	5
17	96	584	86	3.5	0.80	1,548	860	5
18	89	544	105	3.5	1.00	1,161	645	5

TOC total organic carbon, COD chemical oxygen demand, BOD_5 biochemical oxygen demand after 5 days, L_{COD} COD loading factor

5 mg L^{-1}). The influence of the L_{COD} (0.61 and 1.00) on the TOC removal and biodegrad ability enhancement was evaluated. Samples were withdrawn after 0.5, 1 and 5 min. Finally, a set of 16 experiments were carried out by using raw leachate A and B. Leachates A and B were diluted between 16 and 90 % (*v*/*v*) to produce different L_{COD} values ranging from 0.22 to 1.19 (experiments 2, 4–18; Table 1), respectively. Different organic load solutions were prepared, being for leachate A: [TOC]=85±72 mg L^{-1}; [COD]=515±454 mg L^{-1}; [BOD_5]=43±14 mg L^{-1}; and, for leachate B: [TOC]=83±47 mg L^{-1}; [COD]=512±278 mg L^{-1}; [BOD_5]=78±30 mg L^{-1}. The H_2O_2/Fe^{2+} mass ratio and pH were kept constant at 1.8 and 3.5, respectively. The results were used to estimate the relation between biodegradability (in terms of BOD_5/COD or $BOD_5/BOD_{5,0}$) and L_{COD} after 5 min reaction of Fenton process. The same procedure made in the first set of experiments after sampling was followed in the second and last sets of experiments.

2.4 Analysis

TOC was measured using a Shimadzu TOC-VCPH TOC analyzer equipped with an ASI-V autosampler. COD measurements followed the Standard Methods 5220 D (colorimetric method; Clesceri et al. 2005). Although 10 mol. L^{-1} NaOH were added to the samples (eliminating the residual H_2O_2 and its interference on COD analysis), for simplicity, a relationship between TOC and COD of raw leachate was developed and established by analyzing multiple raw leachate samples at various dilutions. So, samples generated during the Fenton oxidation of leachate were analyzed for TOC and the corresponding COD values were obtained using the relationship between TOC and COD (COD=6.18 TOC=0.32; $R^2=0.98$).

BOD measurements followed the Standard Method 5210B (dilution method and thermostated at 20 °C for 5 days; Clesceri et al. 2005). BOD dilution water was freshly prepared for each experiment batch by dissolving Hach® BOD nutrient buffer pillows in ultrapure water in the proportion prescribed by the manufacturer. Dilution water was prepared in a sterile Nalgene carboy and stored in the incubator for up to 24 h prior to setting up a BOD_5 experiment set. On the start day of an experiment, a solution of the inoculum was prepared by following the PolySeed® normal dilution, rehydration and activation procedure. This consisted of one capsule to 500 mL of dilution water placed in a beaker and stirred on a magnetic stirring plate while simultaneously aerating the mix for one hour prior to use. Likewise, the dilution water was also aerated beginning one hour prior to setting up the BOD_5 experiment. Prior to BOD_5 testing, the pH of each sample was adjusted to 7.0±0.2 by using small volumes of 9 mol. L^{-1} H_2SO_4 and 5 mol. L^{-1} NaOH solutions, as needed. Volumes added to achieve the correct pH were less than 250 μL per sample. Aliquots of the samples leachate were measured with a pipette and placed directly into the BOD bottles. Each bottle was then successively filled with a portion of the BOD dilution water, 4 mL of the PolySeed® solution, and BOD dilution water filling the bottle half-way up to the etched bottle's neck. Before carrying out the analyses of BOD_5 to the samples obtained during application of the Fenton process, a previous study was done to evaluate the effect of the leachate dilution (ranging from 1 to 12 %*v/v*) on BOD_5 analysis. Optimal v/v was determined and used in further analyses. The initial DO measurement was taken immediately after each bottle was filled, after which the stopper was tightly secured on the bottle, and this was placed in the incubator. Final DO measurements were taken after 5 days ± 1 h.

The BOD_5 were computed using the following equation:

$$BOD_5 = \frac{(D_1\text{-}D_2)\text{-}(B_1\text{-}B_2)\cdot f}{P} \tag{6}$$

where BOD_5 is the 5 day biochemical oxygen demand (mg. L^{-1}); D_1 is the DO of the diluted sample immediately after preparation (mg. L^{-1}); D_2 is the DO of the diluted sample after incubation for 5 days ± 1 h at 20 °C (mg. L^{-1}); B_1 is the DO of seeded dilution water blank before incubation (mg. L^{-1}); B_2 is the DO of seeded dilution water blank after incubation (mg. L^{-1}); f is the ratio of seed in sample to seed in blank $= \frac{\%\text{seed in } D_1}{\%\text{seed in } B_1}$; and P is the decimal fraction of sample used $= \frac{\text{mL of sample}}{300\text{ mL}}$

Control samples were prepared and incubated with each experiment's batch to assure compliance with standard test criteria (Clesceri et al. 2005). These control samples consisted of two dilution water blanks, three seed control, and two glucose/glutamic acid standards. The dissolved oxygen probe was calibrated for each experiment using the two point calibration procedure: with a zero oxygen solution and water-saturated air, as described in the instrument's manual.

3 Results and Discussion

3.1 Leachate Characterization

Major relevant water quality parameters of the leachate samples A and B are shown in Table 2, respectively. In general, the low average values of BOD_5 of leachates A

Table 2 Important relevant parameters of two investigated landfill leachate samples

Parameter	Leachate A	Leachate B
pH	7.8	7.5
Dissolved oxygen (mg. L^{-1})	2.6	2.6
Alkalinity, as $CaCO_3$ (mg. L^{-1})	2,385±35	2,345±57
Total dissolved solids (mg. L^{-1})	7,057±243	19,066±757
Total organic carbon, COD (mg. L^{-1})	318±52	777±73
Chemical oxygen demand, COD (mg. L^{-1})	1,092±151	2,184±50
Biochemical oxygen demand, BOD_5 (mg.L^{-1})	38±10	151±50
BOD_5/COD	0.035	0.069

and B (38 and 151 mg. L^{-1}), and the low biodegradability, in terms of BOD_5/COD ratios (0.035 and 0.069), indicate typical characteristics of a stabilized leachate (Tchobanoglous et al. 1993). Comparing the two leachate samples, the significantly lower initial values of BOD_5 and BOD_5/COD ratio measured in leachate A compared to B are an indication that leachate A contains a larger proportion of more recalcitrant organic pollutants than leachate B.

3.2 Influence of pH on TOC Removal and Biodegradability Enhancement

The effect of pH on the Fenton process (during the first 5 min) of leachate A (50 %*v*/*v*) was studied at a L_{COD} of 0.61 and a mass ratio H_2O_2/Fe^{2+} of 1.8 to evaluate the profile of the leachate TOC removal and the biodegradability enhancement during the reaction time at different pH values (2.0, 3.5 and 6.0).

Figure 1a suggests that the maximum TOC removal efficiency by the Fenton process occurred at pH of 3.5, with a removal efficiency of 61 %, followed by 40 % and 29 % at pH values of 6.0 and 2.0, respectively. At each pH, the TOC removal increased sharply during the initial 1 min of the reaction, and then leveled off until 5 min of reaction. The optimal pH of 3.5 observed in this study is consistent with prior studies, which reported that the optimum pH for

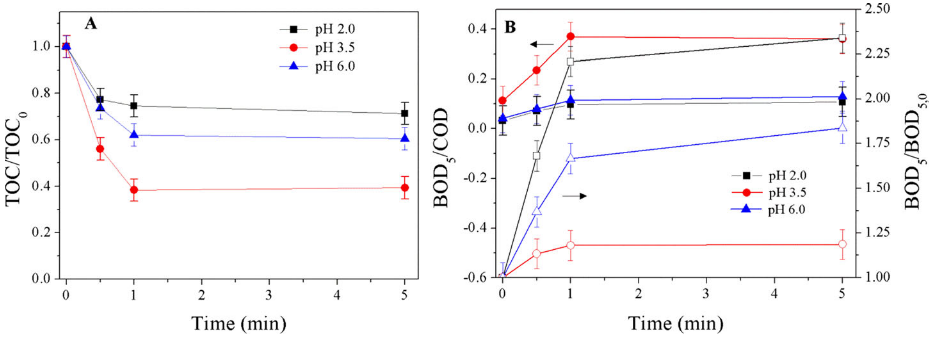

Fig. 1 Influence of the initial pH on the **a** TOC removal and **b** biodegradability enhancement of leachate A, in terms of BOD_5/COD (*solid symbols*) and $BOD_5/BOD_{5,0}$ (*open symbols*) ratios. Initial conditions: [TOC]=85±11 mg L^{-1}; [COD]=515±68 mg L^{-1}; [BOD_5]=30±13 mg L^{-1}; L_{COD}=0.61; H_2O_2/Fe^{2+} (w/w)=1.8; [H_2O_2]=1,782±229 mg L^{-1}; [Fe^{2+}]=990±127 mg L^{-1}

Fenton reactions varied from 2.6 to 3.5 (Pignatello 1992; Nogueira and Guimarães 2000). At extremely low pH (<2.0), the degradation efficiency of TOC decreased due to lower reaction rate of [Fe $(H_2O)]^{2+}$ and scavenging of $^{\bullet}OH$ by H^+ (Nogueira et al. 2007; Machulek et al. 2012). On the other hand, at high pH values (>5.0), the reduction of degradation efficiency was primarily due to increased rate of auto-decomposition of H_2O_2, deactivation of iron ion into iron oxyhydroxides, increased scavenging of $^{\bullet}OH$ by carbonate and bicarbonate, and decreased oxidation potential of $^{\bullet}OH$. During the first minute, Fe^{2+}rapidly catalyzes the formation of $^{\bullet}OH$ from H_2O_2. The hydroxyl radical produced rapidly oxidizes the dissolved organic matter present in the leachate. After 1 min, the concentration of $^{\bullet}OH$ is very low due to limited availability of Fe^{2+}. The regeneration rate of Fe^{2+} (10^{-3}–10^{-2} $M^{-1}.s^{-1}$) is approximately four orders slower than Fe^{2+} consumption (76 $M^{-1}.s^{-1}$) (Eq. 3) (Umar et al. 2010). Therefore, a slower process resulted in the second phase after 5 min of reaction.

A similar behavior was observed for biodegradability enhancement in terms of BOD_5/COD ratio (Fig. 1b). The maximum biodegradability improvement expressed by.

BOD_5/COD ratio increased from 0.11 to 0.37 after 1 min at pH 3.5, while during this same period the average biodegradability increased only from 0.037 to 0.095 at pH 2.0 and 6.0, respectively. The rapid increase of leachate's biodegradability in terms of BOD_5/COD ratio at the initial stage of reaction is consistent with the expected oxidation of larger organic matter, such as humic and fulvic compounds, by high initial concentrations $^{\bullet}OH$. As a result, a larger amount of smaller organic compounds would be produced and result in high BOD_5 (de Morais and Zamora 2005; Batarseh et al. 2007). The magnitude of the biodegradability improvements of this stabilized leachate are also in agreement with data published in the literature for mature landfill leachates. For example, de Morais and Zamora (2005) observed that the Fenton treatment increased leachate biodegradability, e.g., the ratio BOD_5/COD from 0.13 to 0.42. This 223 % increase of BOD_5/COD ratio is comparable with our observed 236 % increase of the BOD_5/COD ratio. In this study, no further improvement of the biodegradability of the leachate (Fig. 1b) after 1 min was observed at all pH values studied, similar to what we had noted for the TOC removal (Fig. 1a).

When biodegradability was measured in terms of $BOD_5/BOD_{5,0}$ ratio, an improvement of this ratio was observed in the order: pH 2.0>6.0>3.5 (Fig. 1b). That is, biodegradability improvement was the lowest when the reaction was conducted at an initial pH of 3.5 followed by pH values of 6.0 and 2.0 (Fig. 1b). At pH of 2.0, BOD_5 increased to more than 2.3 times of the initial BOD_5 after 5 min of Fenton oxidation. At the initially adjusted pH of 3.5 and 6.0, the increase in BOD_5 after the same reaction time was only 1.2 and 1.8 times, respectively. The difference in the biodegradability enhancement, in terms of BOD_5/COD and $BOD_5/BOD_{5,0}$, in relation to pH can be explained based on the results of decreased COD and increased BOD_5 (Table 3). Considering the BOD_5/COD ratio at a pH value of 3.5, although a small increase on the measured BOD_5 was observed, a higher COD removal was noted (Table 3–Exp. 2), yielding a high BOD_5/COD ratio. Although a low TOC and COD removal (Fig. 1a and Table 3–Exp. 1 and 3) were obtained at pH 2.0, more biodegradable oxidized by-products were yielded because the $BOD_5/BOD_{5,0}$ ratio increased significantly (Fig. 1b). These results suggest that the Fenton process can be used at a pH near the neutral value as a pre-treatment method, which would result in the production of biodegradable compounds, thus making the leachate amenable to biological treatment. It is important to emphasize that the value of BOD_5/COD ratio obtained at pH 6 still indicates a leachate containing compounds relatively hard to biodegrade. Although the Fenton process can be applied as a pre-treatment in a wide pH range (between 2.0 and 6.0), all subsequent experiments were conducted at an initial pH of 3.5, due to better TOC removal and biodegradability enhancement in terms of BOD_5/COD. The

Table 3 Results of COD and BOD_5 obtained before and during the Fenton treatment to different initial experimental conditions

Experimental	Sampling time (min)							
	0		0.5		1		5	
	Concentration (mg.L^{-1})							
	COD	BOD_5	COD	BOD_5	COD	BOD_5	COD	BOD_5
1	555	18	425	30	410	40	391	42
2	419	47	227	53	150	56	155	56
3	571	24	416	33	348	40	338	44
4	912	57	568	64	490	72	475	61
5	1,543	30	920	63	937	64	937	89
6	111	27	–	–	–	–	68	30
7	171	36	–	–	–	–	117	43
8	442	50	–	–	–	–	334	52
9	763	72	–	–	–	–	542	89
10	134	36	–	–	–	–	134	25
11	140	30	–	–	–	–	141	29
12	247	55	–	–	–	–	151	83
13	239	42	–	–	–	–	174	46
14	289	39	–	–	–	–	232	45
15	1,155	124	–	–	–	–	874	134
16	460	95	–	–	–	–	241	120
17	584	86	–	–	–	–	436	80
18	544	105	–	–	–	–	424	107

reaction time of 5 min was selected because there was an improvement on the BOD_5 compared to the samples obtained after 1 min (Fig. 1b and Table 3).

3.3 Influence of L_{COD} on TOC Removal and Biodegradability Enhancement

The Fenton reaction can also be significantly influenced by the dose of the chemical reagents, such as Fe^{2+}, H_2O_2, as well as the H_2O_2/Fe^{2+} ratio (Tang 2004). If Fe^{2+} is overdosed, the $^{\bullet}OH$ radical would be scavenged by the Fe^{2+} in excess (De Laat and Gallard 1999), while the excess H_2O_2will also react with the hydroxyl radical without promoting the degradation of organic matter (Nogueira et al. 2007; Melo et al. 2009; Jiang et al. 2010; Trovó et al. 2013). In either cases, the degradation efficiency of leachate will decrease. Therefore, the optimal mass H_2O_2/Fe^{2+} ratio has to be maintained at optimal condition. According to the median of the optimal ratios from the peer reviewed publications statistically analyzed by Singh and Tang (2013), this mass ratio was selected at 1.8 (*w*/*w*) in all the experiments in this study. It should be pointed out that this value can greatly fluctuate according to the type of pollutants and the water quality matrix in the leachate.

When the H_2O_2/Fe^{2+} ratio is maintained constant at 1.8 (*w*/*w*), the steady-state concentration of hydroxyl radical depends upon the dose of H_2O_2. To assess the relationship between TOC removal and biodegradability enhancement during the Fenton process, experiments using two L_{COD} values of 1.00 and 0.61 were performed using leachate A diluted between 16 and 84 % (*v*/*v*), respectively. The initial solutions of the leachate used were prepared at different COD loads: ([TOC]=109±39 mg L^{-1}; [COD]=665±246 mg L^{-1}; [BOD_5]=52±5 mg L^{-1}). Since the COD removal has a linear dependence on L_{COD} (Singh et al. 2013), the effect of organic load, L_{COD}, on TOC removal and biodegradability enhancement was experimentally investigated as shown in Fig. 2.

Figure 2a shows that the TOC removal increased as L_{COD} decreased from 1.00 to 0.61. At a lower L_{COD}, a higher amount of H_2O_2, and consequently, a higher steady-state concentration of hydroxyl radical was available for oxidizing the OM in leachate. When the L_{COD} increased from 0.61 to 1.00, the TOC removal decreased from 60 to 40 % (Fig. 2a) after 1 min, and leveled off up to 5 min. The same behavior was observed for biodegradability enhancement in terms of BOD_5/COD or $BOD_5/BOD_{5,0}$ ratios (Fig. 2b). When L_{COD} increased from 0.61 to 1.00, the improvement of biodegradability in terms of BOD_5/COD increased after 1 min from 0.11–0.062 to 0.37–0.15, respectively (Fig. 2b). On the other hand, a better improvement of the biodegradability, in terms of measured BOD_5, was obtained at the high L_{COD}value for the first minute. After 5 min, the same behavior as that observed for BOD_5/COD ratio appeared in Fig. 2b. Although a lower TOC removal was obtained at the lower L_{COD} value, the use of this COD loading factor of 0.61 rather than the higher L_{COD} of 1.00 is extremely advantageous when the Fenton process is used for pre-treatment, due to the lower amount of required chemical reagents.

In parallel, a set of sixteen experiments with L_{COD} ranging from 0.22 to 1.19 were conducted to determine the relation between biodegradability enhancement (in terms of either BOD_5/COD or $BOD_5/BOD_{5,0}$) and L_{COD} (Fig. 3) for leachates A and B. Figure 3 shows that when L_{COD} was less than 0.8, the BOD_5/COD ratio increased with decreasing L_{COD}. However, when L_{COD} was greater than 0.8, the BOD_5/COD ratio remained at a relatively constant level. However, the lower COD removal was observed during the experiment using lower L_{COD} (Tables 1 and 3), due to the lower amount of $^{\bullet}$OH available to oxidize the OM.

There was a slight difference in the initial $BOD_{5,0}$ of leachates A and B, as shown in Table 2. For both leachates, the profile of the biodegradability in terms of BOD_5/COD or $BOD_{5,0}/BOD_5$ enhancement followed a linear dependence with L_{COD} (R^2=0.87 and 0.51,

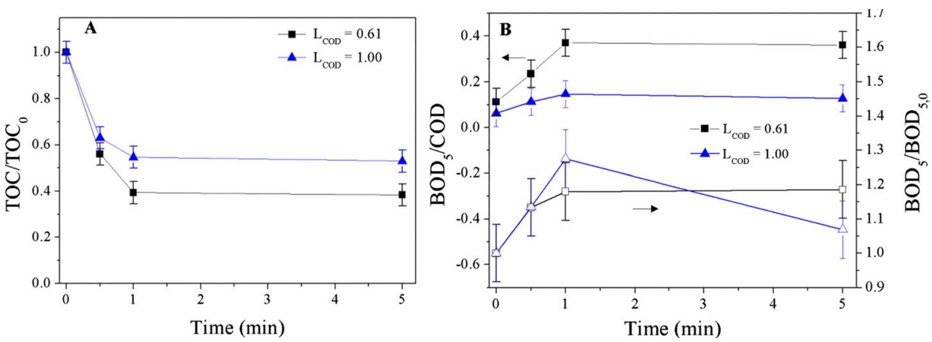

Fig. 2 Influence of L_{COD} on **a** TOC removal and **b** biodegradability enhancement, in terms of BOD_5/COD (*solid symbols*) and $BOD_5/BOD_{5,0}$ (*open symbols*) ratios, of leachate A. Initial conditions: [TOC]=109± 39 mg L^{-1}; [COD]=665±246 mg L^{-1}; [BOD_5]=52±5 mg L^{-1}; H_2O_2/Fe^{2+} (w/w)=1.8; [H_2O_2]=1,701± 243 mg L^{-1}; [Fe^{2+}]=945±135 mg L^{-1}

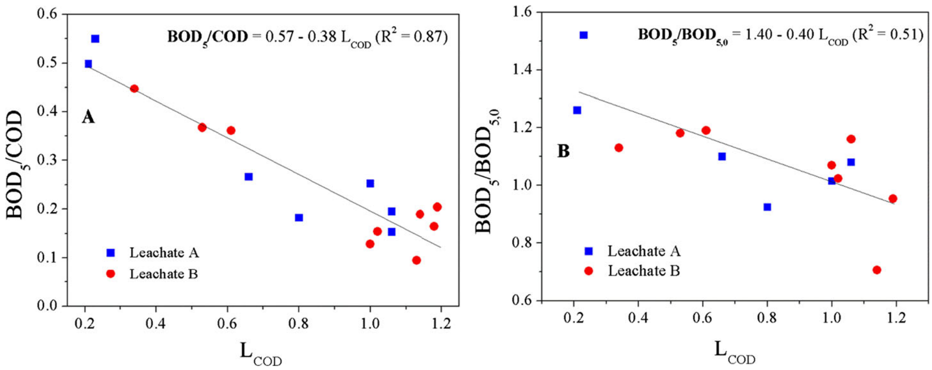

Fig. 3 Relation between the L_{COD} and biodegradability enhancement, in terms of **a** BOD_5/COD and **b** $BOD_5/BOD_{5,0}$, obtained after 5 min of the Fenton process for leachates A and B. Initial conditions: *Leachate A*: [TOC]=85±72 mg L^{-1}; [COD]=515±454 mg L^{-1}; [BOD_5]=43±14 mg L^{-1}; H_2O_2/Fe^{2+} (w/w)=1.8; [H_2O_2]=1,167±816 mg L^{-1}; [Fe^{2+}]=648±453 mg L^{-1}; *Leachate B*: [TOC]=83±47 mg L^{-1}; [COD]=512±278 mg L^{-1}; [BOD_5]=78±30 mg L^{-1}; H_2O_2/Fe^{2+} (w/w)=1.8; [H_2O_2]=1,908±1,287 mg L^{-1}; [Fe^{2+}]=1,060±715 mg L^{-1}

respectively), with slopes of 0.38 and 0.40, respectively (for L_{COD} ranging from 0.22 to 1.19; Fig. 3). The derived equation from the linear regression can be expressed as follows:

$$BOD_5/COD = 0.57–0.38\ L_{COD} \tag{7}$$

Equation (7) presents the relation between BOD_5/COD and L_{COD} with a robust correlation coefficient R^2 of 0.87. It suggests that when L_{COD} approaches zero, the maximum obtainable biodegradability in terms of BOD_5/COD is 0.57, which is about 10 times higher than the average BOD_5/COD of 0.052 for leachates A and B. Theoretically, the Fenton process should reach its maximal efficiency as L_{COD} approaches one. However, as reported by Singh et al. (2013), the maximum efficiency in oxidizing COD occurred at L_{COD} of 0.75 when the H_2O_2/Fe^{2+} mass ratio was 1.8. As a result, the BOD_5/COD ratio should level off starting from 0.75. Figure 3a shows that this initial point apparently started at L_{COD} of 0.8.

Similarly, Eq. (8) shows the statistical correlation between $BOD_5/BOD_{5,0}$ and L_{COD}. Although the correlation of determination R^2 of 0.51 was not as robust as that of Eq. (7), the primary downtrend is confirmed with a negative slope of 0.40.

$$BOD_5/BOD_{5,0} = 1.40–0.40\ L_{COD} \tag{8}$$

Since $BOD_5/BOD_{5,0}$ reflects the ratio of the biodegradable organic compounds after the Fenton process to its initial $BOD_{5,0}$, the maximum obtainable degradability increase would be 1.40 as L_{COD} approaches 0.0 (as suggested by Eq. 8). It is important to note that the value 1.40 only reflects the biodegradable organic portion remaining in the leachate after the Fenton process. Therefore, a maximum $BOD_5/BOD_{5,0}$ of 1.4 is significantly less than ten times BOD_5/COD increase during the oxidation alone. This is because the main portion of oxidized COD was expected to be in the final products, such as CO_2 which does not contribute to BOD_5 of the treated leachate by the Fenton process. In addition, the minimum value of $BOD_5/BOD_{5,0}$ was observed at L_{COD} of 0.8. Since the soluble BOD_5 increase after the Fenton process has to result from COD oxidation, it is not surprised that the slopes of both Eqs. (7) and (8) are similar to the slope for the Fenton process in COD reduction of 0.38, as also reported by Singh et al. (2013).

4 Conclusions

A concomitant improvement of both TOC removal and biodegradability enhancement in terms of BOD_5/COD ratio was observed when the Fenton reaction was performed on mature landfill leachate at the initial pH of 3.5. Our experimental results show that the Fenton process still improves mature leachate biodegradability at pH 6, with an observed BOD_5 increase of 1.8 times its initial value $BOD_{5,0}$. The low value of BOD_5/COD ratio obtained at a pH value of 6 suggests a leachate containing a significant amount of non-biodegradable compounds. High L_{COD} can be employed during pre-treatment of leachate by the Fenton process, since an improvement on biodegradability could be achieved by using relatively lower chemical doses. Leachate biodegradability in terms of BOD_5/COD or $BOD_5/BOD_{5,0}$ ratios was found to decrease linearly with L_{COD} regardless of the initial $BOD_{5,0}$ of leachate samples, with negative slopes of 0.40 and 0.38, respectively. In summary, the Fenton process can be successfully used as a pre-treatment method to improve the biodegradability of mature leachates. Experimental results reported in this study demonstrate that the Fenton process increased the biodegradability of the mature leachate within a short reaction time from 1 to 5 min. To increase biodegradability of a specific mature leachate at a given BOD_5/COD target, Equations (7) and (8), developed in this study, can be used to predict the optimal amount of oxidant, H_2O_2, needed at either the lab-scale or pilot scale, to evaluate the Fenton process as a pre-treatment alternative before biological treatment.

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