Treatment of hazardous landfill leachate using Fenton process followed by a combined (UASB/DHS) system

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ABSTRACT

Fenton process for pre-treatment of hazardous landfill leachate (HLL) was investigated. Total, particulate and soluble chemical oxygen demand (CODt, CODp and CODs) removal efficiency amounted to 67%, 47% and 64%, respectively, at pH value of 3.5, molar ratio (H₂O₂/Fe²⁺) of 5, H₂O₂ dosage of 25 ml/L and contact time of 15 min. Various treatment scenarios were attempted and focused on studying the effect of pre-catalytic oxidation process on the performance of up-flow anaerobic sludge blanket (UASB), UASB/down-flow hanging sponge (DHS) and DHS system. The results obtained indicated that pre-catalytic oxidation process improved the CODt removal efficiency in the UASB reactor by a value of 51.4%. Overall removal efficiencies of CODt, CODs and CODp were 80 ± 6%, 80 ± 7% and 78 ± 16% for UASB/DHS treating pre-catalytic oxidation effluent, respectively. The removal efficiencies of CODt, CODs and CODp were, respectively, decreased to 54 ± 2%, 49 ± 2% and 71 ± 16% for UASB/DHS system without pre-treatment. However, the results for the combined process (UASB/DHS) system is almost similar to those obtained for UASB reactor treating pre-catalytic oxidation effluent. The DHS system achieved average removal efficiencies of 52 ± 4% for CODt, 51 ± 4% for CODs and 52 ± 15% for CODp. A higher COD fractions removal was obtained when HLL was pre-treated by Fenton reagent. The combined processes provided a removal efficiency of 85 ± 1% for CODt, 85 ± 1% for CODs and 83 ± 8% for CODp. The DHS system is not only effective for organics degradation but also for ammonia oxidation. Almost complete ammonia (NH₄-N) removal (92 ± 3.6%) was occurred and the nitrate production amounted to 37 ± 6 mg/L in the treated effluent. This study strongly recommends applying Fenton process followed by DHS system for treatment of HLL.

Key words | advanced oxidation processes (AOPs), DHS, Fenton reaction, hazardous landfill leachate, UASB

INTRODUCTION

Landfilling of hazardous industrial solid wastes is considered the most economical and environmentally acceptable technique all over the world (Deng 2007). However, landfill leachate which is generated due to the percolation of rainfall through wastes and the inherent water content resulting of chemical and biological reactions in waste’s cells leads to serious environmental problems containing pollution of surface water, groundwater, soil and air (Boumechhour et al. 2013). Therefore, treatment of landfill leachate is extremely necessary before discharging it into receiving water bodies to meet the standards and to decrease negative effects on the environment (Badawy et al. 2013). It is well known that landfill leachate contains a large amount of organic compounds (both biodegradable and non-biodegradable), ammonia-nitrogen, heavy metals, inorganic suspended and dissolved matter, high fraction of refractory and large organic molecules such as humic and fulvic acids and other hazardous chemicals (Yoon et al. 1998; Umar et al. 2010). Several treatment techniques have been applied for the treatment of landfill leachates, such as anaerobic and/or aerobic biological degradation (Neczaj et al. 2005; Tamrat et al. 2012), chemical and photo-chemical oxidation (Tauchert et al. 2006; Deng & Englehardt 2007), adsorption (Foo & Hameed 2009), coagulation-precipitation (Vedrenne et al. 2012) and combinations of them (Guo et al. 2010; Cassano et al. 2011). Consequently,
an appropriate treatment technique for an effective treatment of heavily polluted landfill leachate is essential.

Biological methods are usually preferred over physico-chemical ones to remove the majority of pollutants. Usually, the application of a biological treatment process alone is not an option due to the leachate characteristics. Furthermore, neither biological nor chemical treatment separately achieves high treatment efficiencies. There are two reasons for the low removal efficiency of each treatment system: (i) significant presence of high-molecular weight organics that are difficult to remove and (ii) inhibitory effects of organics, inorganic salts and metals to activated sludge microorganisms.

An integrated treatment system was proposed for removal of pollutants from the hazardous landfill leachates (HLLs) in this investigation. Fenton and biological treatment processes or their various combinations were applied: (i) advanced oxidation process with Fe²⁺/H₂O₂ (Fenton’s reagent) to remove/degrade persistent organic compounds and (ii) anaerobic/aerobic biological treatment (up-flow anaerobic sludge blanket/down-flow hanging sponge (UASB/DHS)) system to remove biodegradable components. A promising economical alternative to complete the oxidation of refractory compounds is the use of an advanced oxidation technology with Fe²⁺/H₂O₂ (Fenton’s reagent) as pre-treatment to convert initially bio-recalcitrant compounds into more readily biodegradable intermediates, followed by biological oxidation (UASB/DHS) process of these intermediates to biomass and water. Advanced oxidation processes (AOPs) are among the most powerful methods to deal with the refractory organic constituents, and the Fenton reagent has been considered promising for landfill leachate treatment which can remove colour, decrease the organic load and improve the biodegradability of refractory organics (Gar Alalm et al. 2015a). Several studies of Fenton process on landfill leachate have been investigated by Zhang et al. (2005), who achieved a 65.9% removal rates for chemical oxygen demand (COD). In Fenton’s reaction, ferrous ions react with hydrogen peroxide to generate a highly reactive hydroxyl radical (HO·) in a very simple and a lower capital cost according to Equation (1). Higher concentrations of metal ions (i.e. ferrous ions) result in the rapid generation of hydroxyl radical. However, ferric ions which were produced in Equation (1) consume hydrogen peroxide (Equation (2)) but in a very slow reaction rate compared to the reaction rate between ferrous ions and hydrogen peroxide (Hermosilla et al. 2009).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet \text{OH} + \text{OH}^- \quad (1)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2 \bullet + \text{H}^+ \quad (2)$$

Several advantages have been gained from producing hydroxyl radical (HO·), which has a very strong oxidation potential: the reduction of organic compounds as COD and increasing the biodegradability for further biological processes. Various anaerobic-aerobic treatment processes have been proposed for treatment of landfill leachate, such as bio-filter (Hongjiang et al. 2009), UASB followed by activated sludge process (Hoiijoki et al. 1996) and sequencing batch reactor followed by UASB (Kennedy & Lentz 2000). In this investigation, a novel technology, namely, down-flow hanging sponge (DHS) system was proposed either for treatment of pre-catalytic oxidation effluent or for the treatment of a-UASB reactor effluent. The DHS system consists of polyurethane foam (sponge), as media in which an active microorganism is attached and fills the porous materials. This packing media offers several advantages such as short hydraulic retention time, high biomass concentration, long sludge residence time (SRT) and small footprint as compared to conventional aerobic bioreactors. Landfill leachate is trickled from the top of the reactor downwards from one segment to another in contact to the atmosphere which increases dissolved oxygen (DO) into the leachate flowing through the reactor, precluding the need for external aeration or other energy inputs.

The main objectives of this study were to: (i) evaluate the effectiveness of Fenton’s process as pre-treatment stage for treatment of HLL, more specifically, to investigate the optimum operational conditions for removing COD (i.e. Fenton molar ratio, dosage concentration, pH, and reaction time); and (ii) assess the performance of different scenarios concerning the treatment of pre-catalytic oxidation effluent via UASB, UASB/DHS and DHS systems for removal of the remaining portions of COD fractions (CODt, CODs and CODp) and the nitrification process.

**MATERIALS AND METHODS**

**Characteristics of HLL**

The HLL used in this study was collected from Nasreya hazardous wastes landfill centre which is situated in Borg El-Arab, Alexandria, Egypt. This landfill usually receives hazardous solid wastes from industry. Nasreya landfill dimensions are 140 × 100 m with total capacity of 40,000 ton. The main characteristics of collected HLL are summarized in Table 1.
Batch experiments were carried out in a beaker with a capacity of 1 L to determine the optimum operational conditions (initial pH, molar ratio (H$_2$O$_2$/Fe$^{2+}$), Fenton’s reagent dosage and reaction time) of Fenton’s treatment process. Four experiments were conducted to determine the optimum operational conditions of Fenton process as follows:

1. Effect of initial pH values: the initial pH of HLL was changed from 2 to 8 using 5 M H$_2$SO$_4$ solution and 5 M NaOH solution. Fenton reagent dosage H$_2$O$_2$ of 15 mL/L (15 mL of 30% (w/w) H$_2$O$_2$ solution per litre of leachate) and Fe$^{2+}$ of 200 mg/L, reaction time of 30 min, stirring speed of 1,000 rpm and settling time of 2 h were kept constant. Finally, pH value was adjusted again to 8 for coagulation and sedimentation. Supernatant was sampled by syringe for analysis.

2. Effect of molar ratio (H$_2$O$_2$/Fe$^{2+}$): a set of experiments was carried out at increasing Fe$^{2+}$ dosage from 0 to 5 g/L at constant H$_2$O$_2$ concentration of 15 mL/L, initial pH of 3.5, reaction time of 30 min, stirring speed of 1,000 rpm and settling time of 2 h.

3. Effect of Fenton’s reagent dosage concentration: all the experiments were carried out at initial pH = 3.5, molar ratio = 5 and reaction time = 30 min, stirring speed = 1,000 rpm and settling time = 2 h.

4. Effect of reaction time on COD$_{t}$ removal at constant optimum conditions (initial pH = 3.5, molar ratio = 5, H$_2$O$_2$ of 25 mL/L, stirring speed = 1,000 rpm and settling time = 2 h).

### Scenarios for treatment of pre-catalytic oxidation effluent

The study is divided into three scenarios to assess the effect of the pre-treatment process on the efficiency of UASB, UASB/DHS and DHS system. Figure 1 shows the scenarios for the treatment process. All processes were operated at an average temperature of 25 ± 5 °C. A laboratory-scale set-up consists of UASB followed by DHS were installed and operated continuously for 8 months for treatment of either HLL or pre-catalytic oxidation effluent. The UASB reactor had a working volume of 10 L with internal diameter of 10 cm and a height of 128 cm. The reactor was initially seeded with 6 L sludge collected from the thickener of a municipal wastewater treatment plant. The inoculums sludge (TS = 51 g/L and VS = 35 g/L) represented 60% of the total reactor volume.

The capacity of the DHS system was 8 L, based on the sponge volume. This DHS is composed of three identical segments connected vertically. The first segment from the top was equipped with 100 sponges with volume of 2.1 L randomly distributed, the second and third segments were equipped with 140 sponges each with volume of 2.94 L. The reactor had three windows of 10 cm height between segments for passive natural aeration. The polyurethane sponge has a dimension of 30 mm in height and a 30 mm diameter at cylindrical shape with the following criteria: void ratio of 0.9, pore size of 0.63 mm, specific surface area of 256 m$^2$/m$^3$ and density of 30 kg/m$^3$.

### Analytical methods

The performance of the treatment processes was recorded by analysing samples of landfill leachate influents and effluents of each treatment step, twice a week. pH, COD, total suspended solids (TSS), volatile suspended solids (VSS), ammonia-nitrogen (NH$_4$-N) and total Kjeldahl nitrogen (TKN) were carried out according to APHA (2005). The samples were filtered using 0.45 μm filters (Whatman, UK) to determine soluble COD. The particulate COD was calculated by the difference between total COD and soluble COD.

### RESULTS AND DISCUSSION

### Fenton pre-treatment process

The results in Table 1 show that the VSS/COD ratio ranged from 0.06 to 0.31 with an average value of 0.14 which strongly indicated the low biodegradability of HLL. The effectiveness of the Fenton’s reagent (Fe$^{2+}$ + H$_2$O$_2$) for the pre-treatment of a HLL was investigated for improvement...
of its biodegradability, to be compatible with biological treatment. The effect of pH, molar ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), reagent’s dosage and reaction time on the CODt removal efficiencies were conducted.

Effect of pH

Initial pH is one of the main factors affecting the oxidation of organic substances found in landfill leachate wastewater using Fenton reaction because of its significant influence on the activity of the oxidant and the substrate controlling the hydroxyl radical (HO$^-$) production (Zhang et al. 2005). Figure 2(a) shows the effect of initial pH value on CODt removal efficiency. The results showed that the CODt removal efficiency increased from 15% to 29% at increasing pH values from 2 to 3, respectively. The CODt removal efficiency remained unaffected at increasing pH values from 3 to 4 as shown in Figure 2(a). However, at pH values exceeding 4, the CODt removal efficiency was decreased, resulting in removal efficiency of 26% at pH values of 5 and 6. These results are similar to those reported by Deng (2007), who found that maximum COD removal efficiencies occurred at pH ranging from 2.5 to 3.5 for treatment of municipal landfill leachate using Fenton oxidation process.

Effect of molar ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$)

In Fenton pre-treatment process, increasing $\text{H}_2\text{O}_2$ concentrations enhances organics degradation and $\text{Fe}^{2+}$ ions accelerate the reaction process. However, excessive $\text{H}_2\text{O}_2$ generates gas bubbles and inhibits sludge settling. Furthermore, an excess of $\text{Fe}^{2+}$ ions increases the concentration of total dissolved solids and electrical conductivity in the pre-treated effluent. Determination the optimum value of molar ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is necessary to avoid scavenging reactions (3) and (4) occurring as a result of excess amounts of both reagents (Lopez et al. 2004).

$$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{OH}^-$$ (3)

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} + \text{OH}^-$$ (4)

The results in Figure 2(b) show the efficiency of CODt removal from HLL at different dosages of $\text{Fe}^{2+}$. The results revealed that increasing the dosage of $\text{Fe}^{2+}$ substantially improved the degradation of organic compounds. The removal efficiencies of CODt increased from 21% to 36% by increasing the dosage of $\text{Fe}^{2+}$ from 0.2 g/L to 2 g/L, respectively. Nevertheless, further increases in $\text{Fe}^{2+}$ dosage achieved a slight improvement as shown in Figure 2(b). The results obtained indicated that the optimum molar ratio ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is 5 [i.e. $\text{Fe}^{2+} = 2$ g/L and $\text{H}_2\text{O}_2 = 15$ mL/L].

Effect of Fenton reagents’ dosage ($\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$)

Figure 2(c) shows the effect of increasing the dosages of Fenton reagents ($\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$) on the efficiency of
CODt removal. The results revealed that the CODt removal efficiency increased regularly with increasing the amount of \( \text{H}_2\text{O}_2 \). The removal efficiencies of CODt increased from 34% to 66% by increasing the dosage of \( \text{H}_2\text{O}_2 \) from 2 mL/L to 25 mL/L, respectively. This is mainly due to the abundance of hydroxide radical (HO\(^-\)) which is caused by the existence of higher \( \text{H}_2\text{O}_2 \) concentration (Gar Alalm et al. 2015c). However, further increase in \( \text{H}_2\text{O}_2 \) dosage from 25 mL/L to 35 mL/L slightly increased the CODt removal from 66% to 69%, because the residual of \( \text{H}_2\text{O}_2 \) after Fenton process represented a portion of the residual COD in the treated effluent (Gar Alalm et al. 2015b). Residual hydrogen peroxide concentration was in the range of 0.1–0.3 mL/L at molar ratio of 5 and initial \( \text{H}_2\text{O}_2 \) dosage of 25 mL/L, which was negligible for COD contribution in the treated effluent. The subsequent biological treatment efficiency will be unaffected by the residual values of hydrogen peroxide concentrations where it was less than 2.3 mL/L in the influent (Larisch & Duff 1997).

**Effect of reaction time**

Figure 2(d) shows the effect of reaction time on the CODt removal efficiency from HLL. The results obtained indicated that the organic materials in terms of CODt were drastically degraded by Fenton’s reagent in the first 15 min. The CODt removal efficiency was 67% at a reaction time of 15 min. The removal efficiency of CODt was almost kept constant at a reaction time exceeding 15 min. Based on these results, the optimum reaction time is considered to be 15 min for further experiments. Zhang et al. (2005) found that the most organics removed from landfill leachate occurred in the first 20 min using Fenton process. Figure 2(e) shows the efficiency of Fenton process at optimum operational conditions for removal of COD fractions (CODt, CODs and CODp). 67 ± 3%, 64 ± 3% and 47 ± 12% of CODt, CODs and CODp were removed, respectively, at pH value of 3.5, molar ratio (\( \text{H}_2\text{O}_2/\text{Fe}^{2+} \)) of 5, \( \text{H}_2\text{O}_2 \) dosage of 25 mL/L and contact time of 15 min.

**Scenarios for the treatment of pre-catalytic oxidation effluent**

**First scenario: effect of the pre-catalytic oxidation process on the performance of UASB reactor**

The results in Figure 3(a) show the removal efficiency of CODt in UASB reactor and the combined process consisting of Fenton reagent and UASB reactor. The results obtained
indicated that pre-catalytic oxidation process improved the CODt removal efficiency by a value of 51.4%. This can be explained by the fact that Fenton process is very efficient for reduction of refractory organic compounds and substantially improved biodegradability of landfill leachate where VSS/COD ratio was increased from 0.14 to 0.38 in the pre-catalytic oxidation effluent. Similar trends were observed for the removal of CODs and CODp (Figure 3(b) and 3(c)). The removal efficiencies of CODs and CODp were significantly improved and increased from 5 ± 3% and 26.1 ± 12.2% for UASB to 60.7 ± 6.5% and 55.3 ± 16.1% for Fenton process followed by UASB reactor, respectively. Likewise, the removal efficiency of TSS and VSS was substantially increased for Fenton process followed by UASB reactor as shown in Figure 3(d). The TSS and VSS removal efficiencies were 10 ± 11% and 44 ± 24.6 for UASB and 47.7 ± 16.8% and 59.4 ± 9.6% for the combined process, respectively. A higher removal efficiency of TSS (78%) was obtained by Di Iaconi et al. (2006) in a periodic bio-filter with granular biomass (SBBGR) treating mature municipal landfill leachate.

Second scenario: effect of the pre-catalytic oxidation process on the performance of the combined system consisting of UASB reactor followed by the DHS system

The results presented in Figure 3(a)–3(c) show the effect of pre-catalytic oxidation process on the performance of the combined system (UASB/DHS) in terms of COD fractions (CODt, CODs and CODp). The removal efficiencies of CODt, CODs and CODp were significantly improved for treatment of pre-catalytic oxidation effluent as compared to HLL. Overall removal efficiencies of CODt, CODs and CODp were 80 ± 6%, 80 ± 7% and 78 ± 16% for UASB/DHS treating pre-catalytic oxidation, respectively. The overall removal efficiencies of CODt, CODs and CODp were decreased to 54 ± 2%, 49 ± 2% and 71 ± 16% for UASB/DHS system, respectively, without pre-treatment. However, the results for the combined process (UASB/DHS) system is almost similar to those obtained for UASB reactor treating pre-catalytic oxidation effluent (Figure 3(a)–3(c)). Figure 4 shows the nitrification efficiency in the DHS system. Despite the ammonia being increased in the UASB reactor effluent, the aerobic DHS system was very effective for the nitrification process. However, the ammonia removal efficiency in the UASB/DHS treating pre-catalytic oxidation effluent was increased by a value of 16% as compared to UASB/DHS treating HLL. The nitrate was 35 ± 11 mg/L and 44 ± 9 mg/L in the effluent of UASB/DHS treating HLL.
and UASB/DHS treating pre-catalytic oxidation effluent, respectively.

**Third scenario: effect of the pre-catalytic oxidation process on the performance of the DHS system**

The performance of UASB reactor for treatment of HLL was not satisfactory, as shown in Figure 3(a)–3(c). Moreover, the major portion of COD fractions (CODt, CODs and CODp) was removed in the DHS system treating UASB reactor effluent. Therefore, the effect of the pre-catalytic oxidation process on the performance of the DHS system was extensively investigated. The HLL was continuously fed to the DHS system without Fenton pre-treatment for 45 days and operated at an HRT of 17 h and organic loading rate (OLR) of 4.88 gCOD/L.d. The data in Figure 3(a)–3(c) reveal that the DHS system was effective for COD fractions (CODt, CODs and CODp) removal from HLL. The DHS system achieved average removal efficiencies of 52 ± 4% for CODt, 51 ± 4% for CODs and 52 ± 15% for CODp. This high performance can be attributed to the long SRT of 123 days imposed on the DHS system. A higher COD fractions removal was obtained when HLL was pre-treated by Fenton reagent. The combined processes provided a removal efficiency of 85 ± 1% for CODt, 85 ± 1% for CODs and 83 ± 8% for CODp. This is mainly due to the ability of Fenton pre-treatment process to remove a big portion of organic matter, improve the biodegradability and, therefore, enhance the subsequent biological treatment process. The data in Figure 4 show that the DHS system was not only effective for organics removal but also for ammonia oxidation. The results showed that an almost complete ammonia (NH4-N) removal (92 ± 3.6%) occurred and the nitrate production amounted to 37 ± 6 mg/L in the treated effluent. The removal of ammonia exceeding 96.6 ± 2.6% was recorded for the DHS system treating pre-catalytic oxidation effluent at OLR of 2.4 gCOD/L.d (Figure 4). The major portion of organics in a particulate form was removed using Fenton process which positively affected the nitrification process of the DHS system. Similar results were achieved by Tawfik et al. (2011) and Mahmoud et al. (2011). Ammonia removal efficiency was 91 ± 22% in the DHS system treating grey wastewater at HRT of 11.7 h and OLR of 1.9 gCOD/L.d.

In an attempt to investigate the mechanism removal of organics and the nitrification process in the DHS system, COD fractions and ammonia removal along the height of reactor were extensively described as shown in Figure 5(a)–5(c).
The big portion of CODt (39%), CODs (34%) and CODp (43%) were removed in the first segment of the DHS system treating pre-catalytic oxidation effluent. Little additional removal of COD fractions occurred in the second and third segments (Figure 5(a)). This could be due to most of the organic compounds being adsorbed/degraded by heterotrophic bacteria where the imposed OLR is relatively high in the upper portion of the reactor. As a result, the second segment and third segment received lower OLRs which are favourable for nitrifying bacteria to be dominant over heterotrophs. The DO in the first, second and third segments were 2.1 mg/L, 2.2 mg/L and 4.5 mg/L, respectively. 70% of ammonia (NH₄-N) was oxidized in the combined second and third segments (Figure 5(b)). The NOx-N was 11, 23 and 32 mg/L in the effluent of the first, second and third segments. Figure 5(c) shows that TSS and VSS removal mainly occurred in the upper portion of the reactor, which also plays a key role for the dilution of nitrifiers in the first segment of the DHS system.

**CONCLUSIONS**

Fenton’s pre-treatment process is very efficient for the reduction of organic compounds and substantially improved biodegradability of HLL. The optimum conditions were: pH value of 3.5, molar ratio (H₂O₂/Fe²⁺) of 5, H₂O₂ dosage of 25 mL/L and contact time of 15 min. The performance of UASB reactor for treatment of HLL is extremely low. However, the efficiency of the UASB reactor was substantially improved for treatment of pre-catalytic oxidation effluent. Fenton process followed by the DHS system is the best scenario for the treatment of HLL, resulting the highest removal efficiencies, i.e. CODt of 85 ± 1%, CODs of 85 ± 1%, CODp of 83 ± 8% and ammonia removal of 97%.

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**REFERENCES**


