Removal of Organic Pollutants From Stabilized Landfill Leachate by Fenton Coagulation and Fenton Like Process Process Modeling and Optimization

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Abstract

The treatment of stabilized landfill leachate (SLL) by conventional biological treatment is often inefficient due to the presence of bio-recalcitrant substances. In this study, the feasibility of coagulation-flocculation coupled with the Fenton reaction in the treatment of SLL was evaluated. The efficiency of the selected treatment methods was evaluated through total organic carbon (TOC) removal from SLL. With ferric chloride as the coagulant, coagulation-flocculation was found to achieve the highest TOC removal of 71% at pH 6. Then, the pretreated SLL was subjected to the Fenton reaction. Nearly 50% of TOC removal was achieved when the reaction was carried out at pH 3, H_2O_2:Fe^{2+} ratio of 20:1, H_2O_2 dosage of 240 mM and 1 h of reaction time. By coupling the coagulation- flocculation with the Fenton reaction, the removal of TOC, COD (chemical oxygen demand) and turbidity of SLL were 85%, 84% and 100%, respectively. The ecotoxicity study performed using zebrafish revealed that 96 h LC_{50} for raw SLL was 1.40% (v/v). After coagulation-flocculation, the LC_{50} of the pretreated SLL was increased to 25.44%. However, after the Fenton reaction, the LC_{50} of the treated SLL was found to decrease to 10.96% due to the presence of H_2O_2 residue. In this study, H_2O_2 residue was removed using powdered activated charcoal. This method increased the LC_{50} of treated effluent to 34.48% and the removal of TOC and COD was further increased to 90%. This finding demonstrated that the combination of the selected treatment methods can be an efficient treatment method for SLL.

Keywords: Physicochemical, ecotoxicity, advanced oxidation process, water treatment, total organic carbon, zebrafish

Introduction

Rapid economic transition and urbanization have accelerated municipal solid waste (MSW) generation in growing nations (Guerrero et al., 2013). Among various waste management meth- ods, landfilling is still the preferred method for MSW manage- ment in most of developing countries (Samsudin and Don, 2013). The main disadvantage of landfilling is the production of a huge amount of landfill leachate as one of the toxic by-products. The chemical characteristics of landfill leachate include a high con- tent of organic substances, ammonia, suspended solid, heavy metals, inorganic salts, etc. (Bashir et al., 2015). Therefore, improper management of landfill leachate causes various nega- tive effects on the environment and living organisms (Gupta et al., 2015). Conventional landfill leachate treatment involves a few processes, such as physicochemical, biological and physical treatments (Ahmed and Lan, 2012; Gupta et al., 2014; Liu et al., 2015; Wang et al., 2012). These treatment methods are required in order to ensure the treated leachate meets the stringent water quality standard set by the local authority. On the other hand, researches have also found that the treatment of stabilized landfill leachate (SLL) by conventional biological treatment is inefficient due to the presence of bio-recalcitrant substances (Amor et al., 2015; Oloibiri et al., 2014; Rahim Pouran et al., 2015).

Among various advanced oxidation processes (AOPs), the Fenton reaction has been frequently applied in the full-scale treat- ment of wastewaters from the chemical, food, textile, pharmaceu- tical, pulp and paper industries (Durán et al., 2015; Expósito et al., 2016; Garcia-Ballesteros et al., 2016; Lucas et al., 2012; Pérez et al., 2017; Verma et al., 2012). This method applies H_2O_2 as an oxidizing reagent and iron (II) (Fe^{2+}) as a catalyst to generate the hydroxyl radical (•OH) (Moradi and Ghanbari, 2014). Due to low energy consumption and modest integration with other treatment methods, the Fenton reaction has been widely used in full-scale wastewater treatment (Bautista et al., 2007). One of the leachate treatment methods that has been extensively studied in recent years is the combination of coagulation-flocculation and the Fenton reaction (Amor et al., 2015; Li et al., 2016; Moradi and Ghanbari, 2014; Wang et al., 2009).

The results showed that around 56–89% of chemical oxygen demand (COD) was success- fully removed by this treatment method. Based on a literature review, most of these studies utilized the COD as the main param- eter to evaluate the efficiency of the treatment method. However, high efficiency in COD removal may not represent the removal of the total organic content of leachate, since COD only represents the fraction of oxidizable organic compounds. In this study, total organic carbon (TOC) was used to monitor the efficiency of the selected treatment method. TOC is a better parameter, since it measures the total organic fraction in leachate directly (The Environmental & Protection Agency, 2001). The excellent perfor- mance of the combination of coagulation-flocculation and the Fenton reaction for leachate treatment was revealed in earlier studies (Guo et al., 2010; Klamerth et al., 2013; Li et al., 2016; Liu et al., 2015; Sindhi and Mehta, 2014; Zhang et al., 2005); how- ever, most of these studies were focused on the COD removal without evaluating the toxicity of the treated leachates. So far, several methods have been applied to assess the toxicity of coag- ulation-flocculation and Fenton reaction treated leachate. These methods included the measurement of toxicity using plants (rad- ish, cress, tomato, wheat), bacteria (*Vibrio fischery*), brine shrimp (*Artemia salina*), etc. (Moradi and Ghanbari, 2014; Vedrenne et al., 2012; Žgajnar Gotvajn et al., 2011). For the Fenton reaction, the toxicity of treated leachate to *Vibrio fischery* was found to increase after treatment. In contrast, the phytotoxicity of the lea- chate was found to decrease after treatment (Moradi and Ghanbari, 2014; Vedrenne et al., 2012). This result indicated that different living organisms may respond differently to the toxicity of the tested substances. Therefore, multi-species is crucial for evaluat- ing toxicity variation during treatment processes (Kuang et al., 2013). Since the treated SLL effluents are often released into the aquatic system, fish species are one of the aquatic organisms that are exposed to the treated SLL. So far, the toxicity of treated SLL effluent on fish species has seldom been reported. Therefore, in this study, the zebrafish (*Danio rerio*) was used to evaluate the toxicity of the treated SLL that was produced from each treatment process. The zebrafish has been classified as a model vertebrate for chemical (Hill et al., 2005) and aquatic toxicity (Laura et al., 2014). As reported by Hollert and Keiter (2015), numerous criti- cal pathways that regulate vertebrate development are highly con- served between humans and zebrafish and, therefore, zebrafish also can be used as a prominent model organism for the study of health risks of pollutants in humans and the environment.

Residual H_2O_2 after Fenton treatment is harmful to many organ- isms and will affect the toxicity of effluents (Babuponnusami and Muthukumar, 2014). Reducing reagents are frequently added to the treated industrial wastewater to reduce the remaining H_2O_2 before discharging it into the environment (Olmez-Hanci et al., 2014). Instead of chemical addition, this study utilized the adsorption pro- cess using activated charcoal as an adsorbent for the removal of H_2O_2 residue. Recent literature has showed that organic pollutants can be removed efficiently by activated charcoal.

However, the main drawbacks of this method are high activated charcoal con- sumption and difficulty in regeneration (Li et al., 2010). Therefore, in order to avoid the saturation of activated charcoal by the organic content, the adsorption process was applied after Fenton treatment to minimize the activated charcoal consumption. So far, the applica- tion of the coagulation-flocculation-Fenton reaction coupled with activated charcoal adsorption has not been reported elsewhere.

The objectives of this study were (1) to assess the efficiency of coagulation-flocculation and Fenton treatment in the removal of TOC, COD and turbidity of SLL and (2) to evaluate the toxic- ity of the treated SLL using zebrafish. In this study, SLL was first pretreated with coagulation-flocculation followed by the Fenton reaction. Then, residual H_2O_2 was removed by using activated charcoal without the addition of a reducing reagent. The toxicity of the SLL and the treated SLL on zebrafish was evaluated and reported as lethal concentration (LC_{50}) after 96 h exposure.

Material and methods

Landfill leachate

SLL was obtained from a sanitary landfill located in the state of Selangor (Malaysia). The SLL was collected from the first sedi- mentation pond just before biological treatment. The collected sam- ple was kept in 20 l plastic container and stored at 4°C before use.

Reagent and chemicals

Aluminium sulphate ($Al_2(SO_4)_3$) and poly-aluminium chloride (PACL) were obtained from Sigma Aldrich and R&M Marketing, respectively. Ferric chloride ($FeCl_3$), hydrogen peroxide (H_2O_2), ferrous sulphate heptahydrate (Fe_2SO_4□$7H_2O$), sulphuric acid (H_2SO_4) and activated charcoal were purchased from Merck (Darmstadt Germany).

Instrumental analysis

All physicochemical parameters of SLL, such as turbidity, pH and COD, were determined according to the standard methods published by APHA, AWWA, WEF (2012). TOC measurement was performed using a TOC analyser (TOC-L, Shimadzu, Japan).

Coagulation-flocculation experiment

Coagulation-flocculation treatment was performed using stand- ard jar test apparatus (JLT6 Velp, Scientifica) equipped with six 1 l beakers at room temperature. Experiments were carried out using 500 ml of SLL with $FeCl_3$, $Al_2(SO_4)_3$ and PACL as the coagulant. TOC removal efficiency was examined using three different coagulant dosages (3, 5 and 7 g l^{-1}) at pH values ranging from 5 to 8. During the jar test, the mixture was first vigorously stirred for 2 min at 200 rpm, followed by slow mixing for 30 min at 50 rpm.

Then, stirring was stopped and the floc was left to set- tle for 1 h. The pH of the SLL was adjusted using concentrated H_2SO_4 and/or 5M NaOH. The pretreated effluent that was produced from the best condition was filtered through a sand filter to remove the remaining floc before the Fenton reaction.

Fenton reaction

All Fenton reactions were carried out in batch mode at room tem- perature. The experiment was started with the addition of 25 ml of the pretreated SLL into a 30 ml glass vial. The pH of the efflu- ent was adjusted using H_2SO_4 and/or NaOH. Then, H_2O_2 and Fe_2SO_4 were added and the mixtures were shaken using an orbital shaker at 150 rpm. The final effluent was adjusted to pH 7 by using NaOH before TOC determination. To study the effect of reaction time, the Fenton reaction was carried out for 0.5, 1, 3, 5, 8, 24, 48 and 72 h. For the effect of H_2O_2:Fe^{2+}, H_2O_2 dosage and pH, the Fenton reaction was performed at 1 h reaction times. All the data were analysed using the descriptive statistics method.

H_2O_2 residue removal

Table 1. Chemical characteristics of stabilized landfill leachate.

Parameters	Values
pH	7.95 ± 0.08
Turbidity (NTU)	520 ± 10

COD (mg l^{-1})	5123 ± 281
BOD_5 (mg l^{-1})	351 ± 36
TOC (mg l^{-1})	1389 ± 227
Ammonium nitrogen (mg l^{-1})	2700 ± 200
TDS (mg l^{-1})	10 ± 2
Conductivity (mS cm^{-1})	21 ± 2
Salinity	13 ± 2
BOD_5/COD	0.07
TOC/COD	0.27

COD: chemical oxygen demand; BOD: biochemical oxygen demand; TOC: total organic carbon; TDS: total dissolved solids.

Result and discussion

Characteristics of SLL

The chemical characteristics of the collected leachate are pre- sented in Table 1. Typical SLL is characterized by a relatively moderate concentration of COD (5000–20,000 mg l^{-1}), a high concentration of ammonium nitrogen (3000–5000 mg l^{-1}), being slightly basic (~7.5) and having low biodegradability (BOD_5/ COD < 0.1) (Foo and Hameed, 2009). The selected landfill lea- chate showed a COD of 5123 mg l^{-1}, ammonium nitrogen con-

The excess H O

was removed using the adsorption method. The centration of 2700 mg l^{-1}, BOD5/COD of 0.07 and pH of 7.95.

2 2

Fenton reaction treated samples were passed through an activated carbon column (inner diameter of 2.2 cm and the height of 30 cm) at the flow rate of 5 ml min^{-1}. The concentration of the remaining H_2O_2 was determined using the iodometric method, as described by Karci et al. (2012). Briefly, 50 ml of treated SLL was transferred into a 250 ml Erlenmeyer flask, then 10 ml of potassium iodide (2% w/v), two drops of ammonium molybdate solution and 10 ml of H_2SO_4 (3.5 M) were added. Then, the concentration of liberated iodine was determined by titrating the mixture with standardized thiosulfate solution (0.001–0.1 M). Starch was used as the indicator.

Ecotoxicity analysis

The fish species used for toxicity analysis was zebrafish. Acute toxicity was performed according to the OECD (2004) standard method. Before the toxicity test, the fish were kept for acclimati- zation for seven days in order to resemble the natural aquatic environment. During the acclimatization period, the zebrafish were fed with commercial fish feed and the feeding was stopped 48 h prior to the acute toxicity testing. Toxicity testing was per- formed on a group of 10 fish in a 5 l test container. Experiments were carried out in triplicate. Control was carried out without the addition of SLL and treated SLL. All experiments were con- ducted for 96 h and no feeding was performed during the experi- ment. The mortality of the fish was recorded every 24 h.

Therefore, the collected leachate can be categorized as SLL. Huo et al. (2008) reported that only leachates with a BOD_5/COD ratio of more than 0.25 are suitable for biological treatment. As a result, physicochemical treatment is often applied for the treat- ment of SLL rather than biological treatment. Therefore, in this study, the collected SLL was first treated using coagulation-floc- culation. Then, the efficiency of the Fenton reaction in the miner- alization of pretreated SLL was evaluated.

Coagulation-flocculation process

Coagulation-flocculation is a crucial pretreatment process to reduce the organic content in the leachate treatment. The effi- ciency of this process improves the effectiveness of subsequent treatment processes by reducing a portion of organic content (Amor et al., 2015). In this study, the effectiveness of three coag- ulants, namely $FeCl_3$, $Al_2(SO_4)_3$ and PACL, in the removal of TOC of the SLL was evaluated at different pH values and coagu- lant dosages (Figure 1).

The results indicated that the concentration of TOC of SLL was significantly reduced after coagulation-flocculation. Coagulant dosage, pH and the type of coagulant were found to influence the efficiency of this pretreatment method (Figure 1). The TOC removal efficiency was found to increase from pH 5 to 6 for all selected coagulants. The highest TOC removal efficiency was achieved at pH 6. At pH 6, the percentages of TOC removal

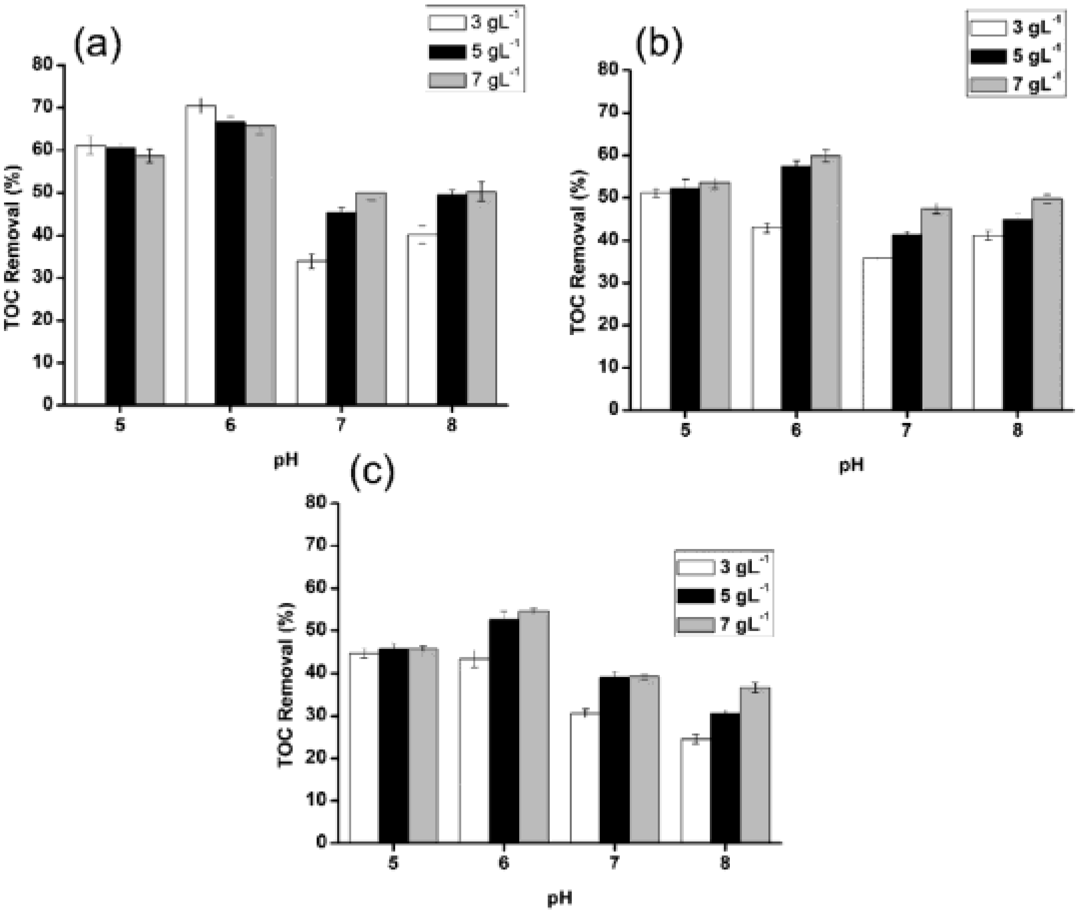

Figure 1. Effect of pH and coagulant dosage on total organic carbon (TOC) removal: (a) $FeCl_3$; (b) poly-aluminium chloride; (c) $Al_2(SO_4)_3$.

were 71%, 60% and 55% for $FeCl_3$, PACL and $Al_2(SO_4)_3$, respec- tively. The efficiency of coagulation-flocculation in the TOC removal was found to decrease with pH after pH 6. In landfill of a polynuclear cation that neutralizes the negatively charged colloid in the SLL leachate, nearly all colloidal particles are negatively charged at pH values of around 5–9 (Duan and Gregory, 2003). The colloi- dal particles are often stable and resistant to aggregates due to the electrical repulsion of the surface charge (Li et al., 2010). The addition of cations from coagulant interacts strongly with the neg- atively charged colloid in the leachate, causing destabilization and coagulation. The effectiveness of coagulation-flocculation in the

$xFe^{3+} + yH\ O$ □ $Fe\ (OH)^{(3x-y)} + yH^+$ $_2$ $_x$ $_y$

$Fe^{3+} + 3OH^-$ □ $Fe(OH)$ $Fe^{3+} + 4OH^-$ □ $Fe(OH)^-$

(1)

(2) $_3$

(3) $_4$

TOC removal is dependent on the pH of the leachate. At different pH values, the coagulant forms different types of hydrolysed spe- cies. For example, Fe^{3+} of $FeCl_3$ transforms into polynuclear cat- ion under the acidic condition (equation (1)), while it can react with the hydroxide ion (OH^-) to form $Fe(OH)_3$ or $Fe(OH)\ ^-$ at the basic condition (equations^4(2) and (3)). The same scenario also occurs for Al^{3+} of $Al_2(SO_4)_3$. By increasing the pH, the hydro- lysed species of Al^{3+} transform from a species with high positive charge to a species with lower positive charge (Li et al., 2010). For PACL, the Al_{13} species is more readily available in a wider pH region due to its high stability (Duan and Gregory, 2003). In this study, the highest TOC removal was mostly achieved at pH

6. Therefore, it can be concluded that a slightly acidic condition favours the coagulation-flocculation process due to the formation

As well as pH, the coagulant dosage was also found to influ- ence the TOC removal efficiency of the coagulation-flocculation process. In general, the percentage of TOC removal was found to increase with increasing coagulant dosage from 3 to 7 g l^{-1}. This observation can be explained by charge neutralization phenom- ena. At the appropriate dosage, a suitable number of cations can neutralize the negatively charged colloid in the SLL and promote the destabilization of the colloidal system during flocculation. When the dosage of the coagulant reaches overdose, the colloid will be stabilized as a result of charge repulsion due to the pres- ence of excess positively charged ions of the coagulant and thus diminishing the effectiveness of coagulation-flocculation in the removal of TOC (Amor et al., 2015; Li et al., 2010). Among the selected coagulants, $FeCl_3$ was found to be the most efficient

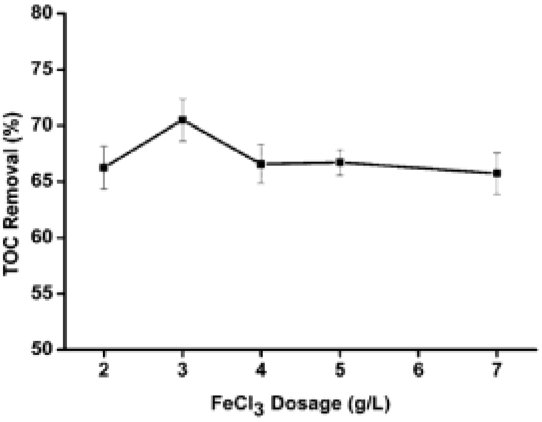

Figure 2. Effect of FeCl

dosage in total organic carbon (TOC)

without the addition of Fe^{2+} (Figure 3(b)). The reduction of TOC was due to the presence of the Fe^{3+} in SLL due to the coagulation- flocculation treatment. Similar to Fe^{2+}, Fe^{3+} also can act as cata- lyst in a Fenton-like reaction to generate •OH from H_2O_2 (Deng and Englehardt, 2006). The TOC removal was found to increase from 16% to 47% with increasing H_2O_2:Fe^{2+} from 1:1 to 20:1 and the Fenton reaction achieved its highest TOC removal at H_2O_2:Fe^{2+} of 20:1. This result showed that the decreased Fe^{2+} enhanced the TOC removal. This was due to the excess Fe^{2+} ions that consumed the •OH (equation (5)). When H_2O_2:Fe^{2+} increased from 20:1 to 30:1, the efficiency of the Fenton reaction in the TOC removal was found to decrease from 47% to 43%. This was due to the insufficient amount of Fe^{2+} to catalyse the Fenton reaction and this consequently reduced the amount of •OH (Babuponnusami and

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removal at pH 6.

Muthukumar, 2014; Deng and Englehardt, 2006)

$Fe^{2+} + \square OH \square Fe^{3+} + OH^-$

(5)

coagulant. This finding was in agreement with the previous reports (Amor et al., 2015; Duan and Gregory, 2003; Li et al., 2010; Ntampou and Zouboulis, 2006). The lower efficiency of PACL as a coagulant might due to the depolymerization of Al_{13} species by natural organic matter (Duan and Gregory, 2003).

The effect of $FeCl_3$ dosage on the removal of TOC was further investigated (Figure 2). The result indicated that 67% of TOC removal was achieved at 2 g l^{-1} of $FeCl_3$. The highest TOC removal of 71% was observed at 3 g l^{-1} of $FeCl_3$. The TOC removal was found to decrease from 71% to 65% when the dos- age of $FeCl_3$ was increased from 3 to 7 g l^{-1}. Consequently, 3 g l^{-1} of $FeCl_3$ was selected to pretreat the SLL at pH 6. The pretreated SLL was treated with the Fenton reaction after sand filtration. To assess the effect of H_2O_2 dosage on the TOC removal, H_2O_2:Fe^{2+} was fixed at 20:1. The concentration of H_2O_2 was var- ied from 30 to 960 mM (Figure 3(c)). TOC removal efficiency was found to increase rapidly from 16% to 52% with increasing the H_2O_2 dosage from 30 to 240 mM. This result was caused by the increased amount of •OH with the increasing concentration of H_2O_2 (Babuponnusami and Muthukumar, 2014). The TOC removal was retarded when the H_2O_2 dosage was increased from 240 and 960 mM. In general, the increasing of H_2O_2 concentra- tion enhanced the TOC removal efficiency (Babuponnusami and Muthukumar, 2014). However, the higher amount of H_2O_2 was also found to scavenge the •OH, as shown in equation (6)

Fenton oxidation process

$H_2O_2 + \square OH \square H_2O + \square H_2O$

(6)

The operating condition of the Fenton process was optimized by varying the reaction time, H_2O_2 to Fe^{2+} ratio (H_2O_2:Fe^{2+}), H_2O_2 dosage and pH. This experiment was started with a study on the variation of TOC removal with reaction time (Figure 3(a)). The result indicated that the TOC removal was increased significantly to 51% for the first 1 h of reaction. No significant TOC removal was observed after 1 h. When the reaction time was increased from 1 to 72 h, the TOC removal only increased by 3%. Therefore, 1 h of reaction time was selected for further study.

H_2O_2:Fe^{2+} is an important parameter for the Fenton reaction to produce a sufficient amount of •OH for water treatment. Fe^{2+} acts as catalyst to generate •OH from H_2O_2, as shown in equation (4) (Lopez et al., 2004)

The effect of pH on the efficiency of TOC removal was eval- uated at pH 2–8. The results indicated that the pH can signifi- cantly influence the efficiency of the Fenton reaction in TOC removal. As shown in Figure 3(d), TOC removal achieved its highest efficiency of 51% at pH 3. Above pH 3, the TOC removal was found to decrease with increasing pH. At higher pH values, self-decomposition of H_2O_2 and precipitation of Fe^{2+} as ferrous hydroxide reduced the amount of •OH (Tang and Huang, 1996). Meanwhile, at pH 2 the TOC removal was also found to be lower than that at pH 3. In this low pH region, the reduction of the efficiency of the Fenton reaction was due to the scavenging effect of •OH by the H^+ ion (Tang and Huang, 1996). In this study, pH 3 was selected as the best pH condition and this result was in agreement with other studies (Amor et al., Fe^{2+} + H O + H^+ □ Fe^{3+} + □ OH + H O (4) 2015; Deng, 2007; Hermosilla et al., 2009; Zhang et al., 2005).

2 2 2

The effect of H_2O_2:Fe^{2+} on TOC removal was examined by varying the concentration of Fe^{2+} from 4 to 120 mM and H_2O_2 concentration was fixed at 120 mM. The experiment was per- formed at pH 3 and the concentration of TOC was monitored at 1 h of reaction time. The result indicated that only 12% of TOC removal was achieved when the Fenton reaction was carried out In order to assess the performance of coagulation-flocculation coupled with the Fenton reaction in the treatment of SLL, the experiment was conducted using the optimized condition of each of the treatment processes. The TOC, COD and turbidity of the treated SLL were measured and the results are outlined in Table 2. It was observed that 71% of TOC, 65% of COD and 90% of turbidity of SLL were successfully removed during

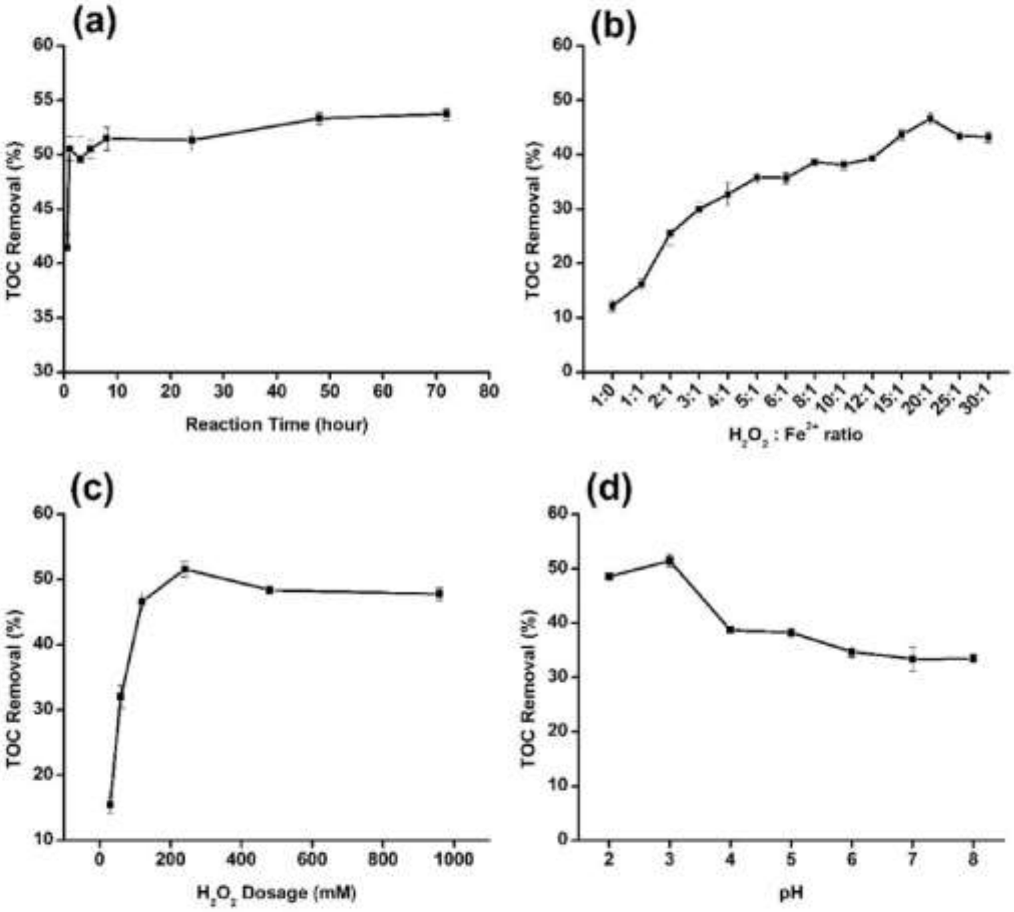

Figure 3. Effect of operating parameters on total organic carbon (TOC) removal: (a) reaction time (dosage of H_2O_2 = 240 mM, pH of leachate = 3, H_2O_2:Fe^{2+} ratio = 20:1); (b) H_2O_2:Fe^{2+} ratio (dosage of H_2O_2 = 240 mM, pH of leachate = 3, contact time = 1 h); (c) H_2O_2 dosage (pH of leachate = 3, H_2O_2:Fe^{2+} ratio = 20:1, contact time = 1 h); (d) pH of leachate (dosage of H_2O_2 = 240 mM, contact time = 1 h, H_2O_2:Fe^{2+} ratio = 20:1).

Table 2. Summary of each treatment processes.

Parameter	% Removal		
	Coagulation-flocculation	Fenton reaction	Overall treatment
TOC	71	50	85
COD	65	55	84
Turbidity	90	100	100

TOC: total organic carbon; COD: chemical oxygen demand.

coagulation-flocculation. The Fenton reaction further enhanced the removal of TOC, COD and turbidity to 85%, 84% and 100%, respectively.

Ecotoxicity

The 96 h LC_{50} of SLL and treated SLL on zebrafish are summa- rized in Figure 4. In this study, the LC_{50} values are presented in % (v/v). Zero mortality was observed in the control group, thereby removing the possibility of experimental interference due to star- vation. It was observed that the LC_{50} of untreated

SLL was 1.4% (v/v). After coagulation-flocculation, the LC_{50} was found to increase to 24.5% (v/v). This result indicated that the pretreated SLL was less toxic than raw SLL. In contrast, after the Fenton reaction, the toxicity of the treated SLL was found to be higher than that of the pre- treated SLL. The LC_{50} for the Fenton reaction treated SLL was 10.96% (v/v). The toxicity of the Fenton reaction was due to the presence of remaining H_2O_2 after Fenton treatment. The residual concentration of H_2O_2 after Fenton treatment was 229.5 mg l^{-1}. It was reported that H_2O_2 residue causes relaxation and constriction of blood vessels, and also possible cell damage to fish and aquatic organisms (Faraci, 2006). Therefore, this result suggested that excess H_2O_2 should be removed from the effluent before dis- charging it into the environment. In industrial wastewater treat- ment, additional chemicals, such as sodium hypochlorite, sodium

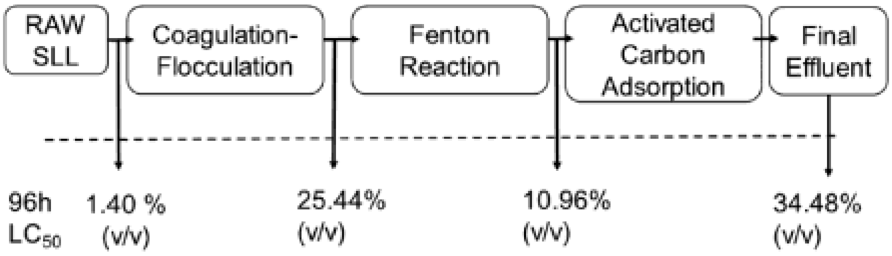

Figure 4. LC_{50} of each treatment process. SLL: stabilized landfill leachate.

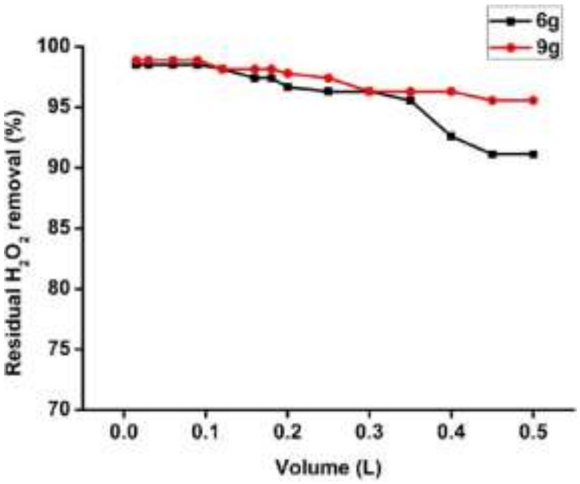

Figure 5. Effect of H_2O_2 removal as a function of volume (l).

thiosulfate and sodium sulphite, are frequently added to reduce the H_2O_2 residual (Liu et al., 2003; Olmez-Hanci and Arslan- Alaton, 2013). These extra chemicals incur additional cost to the water treatment process.

In this study, activated charcoal was used to remove the H_2O_2 residue; the study of such has rarely been reported. As shown in Figure 5, the percentage removal of H_2O_2 by acti- vated charcoal was higher than 90%. At the first 0.12 l, 98% of H_2O_2 removal was achieved for 6 and 9 g of powdered acti- vated charcoal. A slight decrease in efficiency was observed when the volume exceeded 0.12 l. At 0.5 l, the percentage removal of H_2O_2 maintained at more than 90%. Furthermore, the adsorption by activated charcoal was also found to remove the TOC and COD by 30% and 38%, respectively. After acti- vated charcoal adsorption, the LC_{50} of the treated SLL was 34.48%. This result showed that the final treated

SLL was far less toxic than the pretreated and Fenton reaction treated SLL. Alvarez-Vazquez et al. (2004) reported that COD removal by conventional multistage biological treatment is generally less than 60%. In comparison with conventional biological treat- ment for SLL, the selected combination technique provides better organic content removal and produced less toxic efflu- ent. According to the Malaysian Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulation 2009, the concentration of COD for the final leachate effluent is set at <400 mg l^{-1}. In this study, the COD concentration for the final effluent was 361.3 mg l^{-1}. Therefore, it can be concluded that the produced effluent meets the local discharge limit.

Conclusions

The efficiency of coagulation-flocculation coupled with the Fenton reaction for the treatment of SLL was examined. The result demonstrated that coagulation-flocculation coupled with the Fenton reaction is an effective method to remove TOC from SLL. In coagulation-flocculation, 71%, 65% and 90% of TOC, COD and turbidity, respectively, were successfully removed from SLL using $FeCl_3$ as the coagulant. In general, this result indicated that the TOC removal was more favourable when the coagulation-flocculation was performed at a slightly acidic con- dition (pH 6). The pretreated SLL was subjected to the Fenton reaction. The results indicated that the Fenton reaction is an effective oxidation method in reducing TOC of the pretreated SLL. The result showed that 50%, 55% and 100% of TOC, COD and turbidity were removed. However, the ecotoxicity of the Fenton reaction treated SLL was found to be higher than that of the pretreated SLL due to the presence of H_2O_2 residue. This study demonstrated that the H_2O_2 can be removed by using pow- dered activated charcoal without the addition of a reducing rea- gent and, consequently, the ecotoxicity of the treated SLL was reduced. In general, the selected combination of treatment meth- ods can be an effective and efficient alternative method for the treatment of SLL. Since the Fenton reaction has been applied in the full-scale treatment of numerous wastewaters, it could be a potential and practical method for SLL treatment.

Declaration of conflicting interests

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References

1. Ahmed FN and Lan CQ (2012). Treatment of landfill leachate using mem- brane bioreactors: A review. *Desalination* 287: 41–54.
2. Alvarez-Vazquez H, Jefferson B and Judd SJ (2004) Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review. *Journal of Chemical Technology & Biotechnology* 79: 1043–1049.
3. Amor C, De Torres-Socías E, Peres JA, et al. (2015) Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes. *Journal of*

Hazardous Materials 286: 261–268.

4. APHA,AWWA,WEF:2012 (2012) Standard methods for examination of water and wastewater.
5. Babuponnusami A and Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. *Journal of Environmental Chemical Engineering* 2: 557–572.
6. Bashir MJK, Aziz HA, Amr SSA, et al. (2015) The competency of vari- ous applied strategies in treating tropical municipal landfill leachate. *Desalination and Water Treatment* 54: 2382–2395.
7. Bautista P, Mohedano AF, Gilarranz MA, et al. (2007) Application of Fenton oxidation to cosmetic wastewaters treatment. *Journal of Hazardous Materials* 143: 128–134.
8. Deng Y (2007) Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. *Journal of Hazardous Materials* 146: 334–340.
9. Deng Y and Englehardt JD (2006) Treatment of landfill leachate by the Fenton process. *Water Research* 40: 3683–3694.
10. Duan J and Gregory J (2003) Coagulation by hydrolysing metal salts.
11. *Advances in Colloid and Interface Science* 100–102: 475–502.
12. Durán A, Monteagudo JM, Gil J, et al. (2015) Solar-photo-Fenton treatment of wastewater from the beverage industry: Intensification with ferrioxa- late. *Chemical Engineering Journal* 270: 612–620.
13. Expósito AJ, Monteagudo JM, Díaz I, et al. (2016) Photofenton degradation of a beverage industrial effluent: Intensification with persulfate and the study of radicals. *Chemical Engineering Journal* 306: 1203–1211.
14. Faraci FM (2006) Hydrogen peroxide: Watery fuel for change in vascular biol- ogy. *Arteriosclerosis, Thrombosis, and Vascular Biology* 26: 1931–1933.
15. Foo KY and Hameed BH (2009) An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials* 171: 54–60.
16. Garcia-Ballesteros S, Mora M, Vicente R, et al. (2016) Gaining further insight into photo-Fenton treatment of phenolic compounds commonly found in food processing industry. *Chemical Engineering Journal* 288: 126–136.
17. Guerrero LA, Maas G and Hogland W (2013) Solid waste management chal- lenges for cities in developing countries. *Waste Management* 33: 220–232. Guo JS, Abbas AA, Chen YP, et al. (2010) Treatment of landfill leachate using a combined stripping, Fenton, SBR, and coagulation process.
18. *Journal of Hazardous Materials* 178: 699–705.
19. Gupta A, Zhao R, Novak JT, et al. (2014) Application of Fenton's reagent as a polishing step for removal of UV quenching organic constituents in biologically treated landfill leachates. *Chemosphere* 105: 82–86.
20. Gupta N, Yadav KK and Kumar V (2015) A review on current status of municipal solid waste management in India. *Journal of Environmental Sciences (China)* 37: 206–217.
21. Hermosilla D, Cortijo M and Huang CP (2009) The role of iron on the degrada- tion and mineralization of organic compounds using conventional Fenton and photo-Fenton processes. *Chemical Engineering Journal* 155: 637–646.
22. Hill AJ, Teraoka H, Heideman W, et al. (2005) Zebrafish as a model vertebrate for investigating chemical toxicity. *Toxicological Sciences* 86: 6–19.
23. Hollert H and Keiter SH (2015) Danio rerio as a model in aquatic toxicology and sediment research. *Environmental Science and Pollution Research* 22: 16243–16246.
24. Huo S, Xi B, Yu H, et al. (2008) Characteristics of dissolved organic matter (DOM) in leachate with

different landfill ages. *Journal of Environmental Sciences* 20: 492–498.

25. Karci A, Arslan-Alaton I, Olmez-Hanci T, et al. (2012) Transformation of 2,4-dichlorophenol by H 2O 2/UV-C, Fenton and photo-Fenton processes: Oxidation products and toxicity evolution. *Journal of Photochemistry and Photobiology A: Chemistry* 230: 65–73.
26. Klamerth N, Malato S, Agüera A, et al. (2013) Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Research* 47: 833–840.
27. Kuang J, Huang J, Wang B, et al. (2013) Ozonation of trimethoprim in aqueous solution: Identification of reaction products and their toxicity. *Water Research* 47: 2863–2872.
28. Laura C, Ion G, Eugenia O, et al. (2014) Original article assessment of 2, 4-difluoroaniline aquatic toxicity using a zebrafish (danio rerio) model. *Thai Journal of Veterinary Medicine* 44: 445–452. Li J, Zhao L, Qin L, et al. (2016) Removal of refractory organics in nanofiltration concentrates of municipal solid waste leachate treatment plants by combined Fenton oxidative-coagulation with photo - Fenton processes. *Chemosphere* 146: 442–449.
29. Li W, Hua T, Zhou Q, et al. (2010) Treatment of stabilized landfill leachate by the combined process of coagulation/flocculation and powder activated carbon adsorption. *Desalination* 264: 56–62.
30. Liu W, Andrews SA, Stefan MI, et al. (2003) Optimal methods for quenching H_2O_2 residuals prior to UFC testing. *Water Research* 37: 3697–3703. Liu Z, Wu W, Shi P, et al. (2015) Characterization of dissolved organic matter in landfill leachate during the combined treatment process of air stripping, Fenton, SBR and coagulation. *Waste Management* 41: 111–118.
31. Lopez A, Pagano M, Volpe A, et al. (2004) Fenton's pre-treatment of mature landfill leachate. *Chemosphere* 54: 1005–1010.
32. Lucas MS, Peres JA, Amor C, et al. (2012) Tertiary treatment of pulp mill wastewater by solar photo-Fenton. *Journal of Hazardous Materials* 225– 226: 173–181.
33. Moradi M and Ghanbari F (2014) Application of response surface method for coagulation process in leachate treatment as pretreatment for Fenton process: Biodegradability improvement. *Journal of Water Process Engineering* 4: 67–73.
34. Ntampou X and Zouboulis AI (2006) Appropriate combination of physico- chemical methods (coagulation/flocculation and ozonation) for the efficient treatment of landfill leachates. *Chemosphere* 62: 722–730.
35. OECD (2004) OECD 210 fish early life stage toxicity test. *Oecd/Ocde* 220: 1–22. Olmez-Hanci T and Arslan-Alaton I (2013) Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol. *Chemical*
36. *Engineering Journal* 224: 10–16.
37. Olmez-Hanci T, Arslan-Alaton I and Dursun D (2014) Investigation of the toxicity of common oxidants used in advanced oxidation processes and their quenching agents. *Journal of Hazardous Materials* 278: 330–335.
38. Oloibiri V, Ufomba I, Chys M, et al. (2014) A comparative study on the efficiency of ozonation and coagulation-flocculation as pretreatment to activated carbon adsorption when treating biologically stabilized landfill leachate. *Waste Management* 43: 335–342.
39. Pérez JF, Llanos J, Sáez C, et al. (2017) Treatment of real effluents from the pharmaceutical industry: A comparison between Fenton oxidation and conductive-diamond electro-oxidation.

Journal of Environmental Management 195: 216–223.

40. Rahim Pouran S, Abdul Aziz AR and Wan Daud WMA (2015) Review on the main advances in photo-Fenton oxidation system for recalcitrant waste- waters. *Journal of Industrial and Engineering Chemistry* 21: 53–69.
41. Samsudin M and Don MM (2013) Municipal solid waste management in Malaysia : Current practices, challenges and prospects. *Jurnal Teknologi* 62: 95–101.
42. Sindhi Y and Mehta M (2014) COD removal of different industrial waste- water by fenton oxidation process. *International Journal of Engineering Science & Research Technology* 3: 1134–1139.
43. Tang WZ and Huang CP (1996) 2,4-Dichlorophenol oxidation kinetics by Fenton's reagent. *Environmental Technology* 17: 1371–1378.
44. The Environmental, & Protection Agency (2001) Parameters of water qual- ity. *Environmental Protection* 1–133.
45. Vedrenne M, Vasquez-Medrano R, Prato-Garcia D, et al. (2012) Characterization and detoxification of a mature landfill leachate using a combined coagulation – Flocculation/photo Fenton treatment. *Journal of Hazardous Materials* 205–206: 208–215.
46. Verma AK, Dash RR and Bhunia P (2012) A review on chemical coagula- tion/flocculation technologies for removal of colour from textile waste- waters. *Journal of Environmental Management* 93: 154–168.
47. Wang X, Chen S, Gu X, et al. (2009) Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process. *Waste Management* 29: 1354–1358.
48. Wang Y, Li X, Zhen L, et al. (2012) Electro-Fenton treatment of concentrates generated in nanofiltration of biologically pretreated landfill leachate. *Journal of Hazardous Materials* 229–230: 115–121.
49. Žgajnar Gotvajn A, Zagorc-Koncan J and Cotman M (2011) Fenton's oxida- tive treatment of municipal landfill leachate as an alternative to biological process. *Desalination* 275: 269–275.
50. Zhang H, Jin H and Huang C (2005) Optimization of Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials* 125: 166–174.