

Degradation of recalcitrant compounds from stabilized landfill leachate using a combination of ozone-GAC adsorption treatment

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Abstract

Laboratory experiments were undertaken to investigate the treatment performances of ozonation alone and/or its combination with granular activated carbon (GAC) adsorption for raw leachate from the NENT landfill (in Hong Kong). To improve its removal of recalcitrant contaminants from the leachate, the surface of GAC was oxidized with ozone prior to treatment. With respect to ozone dose and pH, the removal of COD and/or NH₃-N from ozonation alone and combined ozone-GAC adsorption were evaluated and compared to those of other physico-chemical treatments in some reported studies. The removal mechanism of recalcitrant compounds by ozone-GAC adsorption treatment was presented. Among the various treatments studied, the combination of ozone-GAC adsorption using ozone-modified GAC had the highest removal for COD (86%) and/or NH₃-N (92%) compared to ozonation alone (COD: 35%; NH₃-N: 50%) at the same initial COD and/or NH₃-N concentrations of 8000 and 2620 mg/L, respectively. Although the integrated treatment was more effective than ozonation alone for treating stabilized leachate, the results suggested that it could not generate treated effluent that complied with the COD limit of lower than 200 mg/L and the NH₃-N discharge standard of less than 5 mg/L. Therefore, further biological treatments to complement the degradation of the leachate are still required to meet the environmental legislation. © 2006 Elsevier B.V. All rights reserved.

Keywords: Advanced oxidation process (AOP); Landfill leachate management; Municipal solid waste; Non-biodegradable compounds; Physico-chemical treatments

1. Introduction

Landfill is one of the most widely employed methods for the disposal of municipal solid waste (MSW) around the world. Up to 95% of the total MSW collected worldwide is disposed of in landfills [1]. More than 150,000 landfills have been built worldwide with over 55,000 and 35,000 sites located in the USA and Germany, respectively [2,3]. In the USA, about 57% of the 218 million tonnes of the MSW generated in 2000 was disposed of in landfills [4], while in China, over 80% of the 160 million tonnes of the municipal refuse generated in the same year was buried in 668 landfills [5].

After being landfilled, the refuse decomposes through a series of combined physico-chemical and biological processes, which may take a period of more than 50 years. During the decomposition process, a highly contaminated wastewater called “leachate”

is generated by excess rainwater percolating through the waste layers in the landfill [6]. The common features of raw leachate from a local landfill are its high concentrations of ammoniacal nitrogen (NH₃-N) (2000–5000 mg/L) and moderately high strength of recalcitrant compounds (as reflected by its COD value) (5000–20,000 mg/L), as well as a low ratio of BOD₅/COD of less than 0.1 [7,8].

Of the toxic pollutants such as adsorptive organic halogen (AOX), heavy metals and xenobiotic compounds that are present in landfill leachate, NH₃-N, resulting from the decomposition process of organic nitrogen, has been identified not only as a major long-term pollutant [9], but also as the primary cause of acute toxicity [10]. Because NH₃-N is stable under anaerobic conditions, it typically accumulates in the leachate [9]. With a concentration of higher than 100 mg/L [11], untreated NH₃-N is highly toxic to aquatic organisms, as confirmed by toxicity tests using zebrafish (*Danio rerio*) [12], *Daphnia magna* [13] and luminescent bacteria [14].

Unless properly treated, leachate that seeps from a landfill can infiltrate and contaminate the underlying groundwater. Once the

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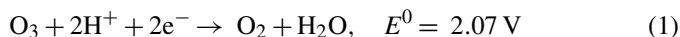
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leachate escapes to the groundwater, it is difficult and expensive to have it controlled and cleaned up, thus posing potentially serious hazards not only to living organisms, but also to public health in the long term. In most cases, it is extremely difficult to restore the polluted groundwater to its former state. In recent years, the risk of groundwater pollution due to leachate seepage has become a major environmental concern worldwide.

A sound engineering design of a landfill can prevent or minimize the leakage of leachate from reaching the groundwater table. Measures include diverting the surface run-off from the site, proper soil cover, proper vegetation and a proper means for leachate interception and collection systems such as synthetic/natural liners, piping and pumping the leachate to a treatment facility [15]. However, most of these precautions can only be applied in newly designed landfills. Some old landfills still generate huge quantities of leachate, which must be treated prior to discharge.

To achieve a satisfactory removal of refractory pollutants from the leachate, several types of physico-chemical treatments such as ammonium stripping, chemical precipitation, coagulation–flocculation, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been employed worldwide. In Hong Kong, leachate from local landfills has been commonly treated on-site using biologically aerobic reactors [16]. Despite reducing the volumetric loading of the reactors, this practice requires a large installation space and high operational cost of US\$ 12.5 m⁻³ of the treated effluent.

As one of the most powerful oxidants with an oxidation potential (E^0) of 2.07 V (Eq. (1)), ozone can act as a very strong oxidizing agent for the treatment of contaminated wastewater of high strength [17]:

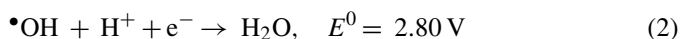


Due to its capability of transforming contaminants into innocuous substances within a short period, ozone has been identified as a potentially effective means to treat landfill leachate. Unlike chlorination, ozonation does not produce any secondary pollutant in the environment, since the ozonation of organic matter in the leachate leads to the formation of low molecular weight compounds such as acetic acid [18].

Because of its large surface area, microporous structure and surface reactivity, GAC adsorption is one of the most attractive methods for the removal of recalcitrant compounds from leachate. Basically, adsorption is a process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [19]. Adsorption treatment using GAC may be technically applicable to meet the increasingly stringent discharge standards for refractory contaminants in developing countries.

In recent years, a combination of ozonation and GAC adsorption has emerged as one of the most promising options for the treatment of contaminated wastewater. Ozone is capable of oxidizing organic substances to their highest stable oxidation states and then, produces CO₂ and H₂O, while GAC can accelerate the kinetic rate of the ozone decomposition through the formation of •OH radicals in the solution [20]. With a high oxidation

potential of 2.80 V, •OH radical is a highly reactive species (Eq. (2)):



Through the •OH radicals, the ozone rapidly reacts with most of the target recalcitrant compounds in the leachate for an ultimate degradation. An integrated treatment of ozonation and GAC adsorption may synergize the advantages of their treatment performance, while overcoming their respective limitations.

In this study, laboratory experiments were carried out to investigate the treatment performances of ozonation alone and/or its combination with GAC adsorption for raw leachate from the NENT landfill (in Hong Kong). To improve its removal of recalcitrant contaminants from the leachate, the surface of GAC was oxidized with ozone prior to treatment. With respect to the ozone dose and pH, the removal of COD and/or NH₃-N from ozonation alone and/or combined ozone-GAC adsorption were evaluated and compared to those of other physico-chemical treatments in some reported studies. The removal mechanism of recalcitrant compounds by combined ozone-GAC adsorption treatment is also presented.

2. Experiments

2.1. Materials and methods

An aged raw leachate was collected from the North East New Territory (NENT) landfill situated in Ta Kwung Lin, a remote part of the New Territories. It is one of the three on-going landfills in Hong Kong SAR, in addition to the South East New Territories (SENT) and the West New Territories (WENT) landfills. With an overall capacity of 37 × 10⁶ m³ and a total area of 61 ha, the NENT landfill receives 3800 tonnes of MSW per day [21] from an urban population of nearly 7.5 million of inhabitants in 2005. Since its first commissioning operation in June 1995, the major component of waste dumped in the landfill is municipal refuse such as domestic, construction and industrial waste. The NENT landfill generates approximately 800 m³ of leachate per day [22].

To study the effects of seasonal variations on the composition and the concentration of the raw leachate from the NENT landfill, the leachate samples were collected in December 2004 (winter) and July 2005 (rainy and summer). In Hong Kong, spring and summer are generally considered as rainy season, while fall and winter are dry seasons. Due to the impacts of rainfall on the change of physico-chemical characteristics of the leachate during the rainy season, the samples collected in December 2004 were used throughout this study.

The samples were collected in 20 L of polyethylene carboys that were filled to the capacity and capped tightly. They were then stored in a refrigerated storage chamber at 4 °C to minimize any further changes that might occur in its physico-chemical and biological properties prior to experiments. The leachate was immediately characterized according to the Standard Methods [23] for the following parameters: pH, COD, BOD₅, NH₃-N, alkalinity (as CaCO₃), total nitrogen, NO₃-N, total

organic carbon (TOC), alkaline metal cations and conductivity. Prior to treatment, the pH of the raw leachate was measured using a pH meter model Orion 710A (The USA). Adjustment of the pH was carried out using 0.1N NaOH and/or 0.1N HCl. The concentration of $\text{NH}_3\text{-N}$ and COD was analyzed by a spectrophotometer model Spectronic 4001 (USA), while the TOC and the conductivity of the leachate were measured by using a TOC analyzer type Shimadzu 5000 A (USA) and/or a conductivitymeter type YSI 63/25 (USA), respectively.

2.2. Surface modification of GAC with ozone

Prior to use, 50 g of GAC type PHO 8/35 LBD (Carbokarn Co. Ltd., Thailand) was placed in a glass beaker. To increase the oxygen-containing functional group of the GAC, the surface of GAC was oxidized with ozone and treated with NaOH. About 0.5 L of 0.1N NaOH was added to the beaker and the suspension was agitated at 200 rpm for 3 h. The samples were then separated from the solution and they were dried in an oven at 105°C for 24 h. The GAC samples were placed in a glass column with an internal diameter (i.d.) of 2 cm and height (h) of 100 cm. The adsorbent was then treated with gaseous ozone at an inflow concentration of 3 mg/L and a flow rate of 1.6 L/min (a mass rate of 4.8 mg/min) for 3 h. The samples were subsequently washed with deionized water, dried in an oven at 105°C for 24 h and stored in a desiccator [24]. The physical characteristics of the adsorbent are presented in Table 1.

2.3. Ozonation of leachate

The ozonation of 0.8 L leachate was carried out at ambient temperature ($25\text{--}27^\circ\text{C}$) in a glass reactor (i.d.: 2 cm; h : 100 cm) by recirculating the leachate from top to bottom. The bottom of

Table 1

Physical properties of the GAC used

Density (g/cm^3)	0.50
Particle size (mm)	0.50
Total surface area (m^2/g)	900–1100
Retail price (US\$/kg)	1.37

the reactor was fitted to a column contactor with a porous glass plate diffuser with $10\text{--}15\ \mu\text{m}$ of pore size. Ozone was generated by an ozone generator model ORVG03 (Hong Kong) using ambient air as the feeding gas and passed into the reactor through the column contactor. In a closed system, the gaseous ozone with a flow rate of 1.6 L/min was continuously fed into the reactor for 30 min. The ozone concentration in the feeding gas was 3 mg/L with a generation rate of 4.8 mg/min. The treated effluent was collected every 5 min to determine the COD and $\text{NH}_3\text{-N}$ concentration [25].

Ozone consumption was measured as the difference between the initial ozone dose applied in the feeding gas and the residual ozone residing in the exhaust gas of the reactor. The residual ozone in the stream was determined by connecting the reactor to a series of impingers containing 1% KI solution (Eq. (3)), while the resulting iodine was titrated by using 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ in the presence of 1% starch aqueous solution as the indicator [26]. The titration was continued until the disappearance of the violet color:



2.4. GAC column adsorption

In a fixed-bed study, the same type of glass column (i.d.: 2 cm; h : 100 cm) was packed with 35 g of an adsorbent (as-received

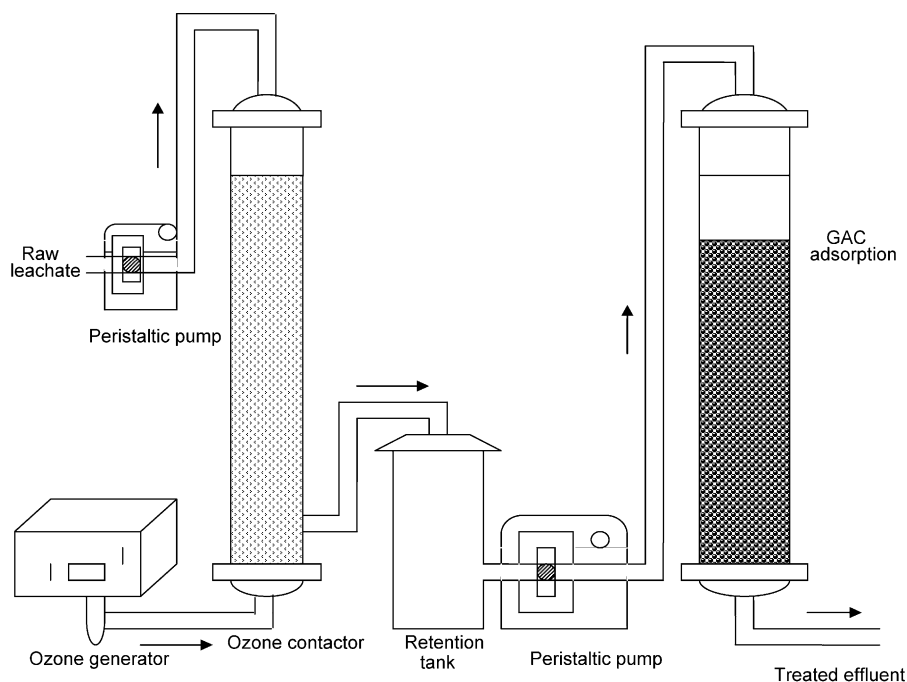


Fig. 1. Scheme of the integrated ozone-GAC adsorption treatment.

GAC and/or ozone-modified GAC). The bottom of the reactor was fitted with 1 cm of glass wool and a glass bead layer. Without pretreatment, the raw leachate passed through the reactor from top to bottom (down-flow mode) at a flow rate of 3 mL/min for a single circulation. The pH of the effluent was recorded every 15 min to monitor any changes that might occur during adsorption. The treated effluent was periodically collected for NH₃-N and/or COD analyses. The column operation was terminated as soon as the saturation point ($C_e/C_0 = 1$) was achieved. C_0 and C_e represent the initial and equilibrium concentrations of NH₃-N and/or COD in the leachate (mg/L), respectively. The same method was also employed for the subsequent treatment of ozonated leachate [27]. Unless otherwise specified, ozone-oxidized GAC was employed in the integrated process. The integrated ozone-GAC adsorption treatment scheme is depicted in Fig. 1.

2.5. Analytical methods

The changes in NH₃-N and/or COD levels were determined colorimetrically according to the Standard Methods [23]. An indophenol-blue color was formed in the reaction between NH₃-N in the leachate sample and alkaline phenol and hypochlorite reagents (Standard Methods 4500F), while the closed reflux colorimetric method was employed for COD determination (Standard Methods 5520D). Absorbance was measured at 626 nm for NH₃-N determination and at 600 nm for COD analyses. The removal efficiency of NH₃-N and/or COD (E) after treatment is defined as

$$E (\%) = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (4)$$

2.6. Statistical analysis

To ensure the accuracy, reliability and reproducibility of the collected data, the experiments were carried out at least in triplicate and the mean value of the three data sets is presented. If the relative error exceeded 1.0%, the data would be disregarded and a fourth experiment conducted until the error fell within

the acceptable range. All statistical tests were performed using SPSS 11.00 Windows version with a confidence interval (CI) of 95%. Differences were considered statistically significant when $p \leq 0.05$.

3. Results and discussion

3.1. Leachate characteristics from the NENT landfill

The characteristics of raw leachate from the NENT landfill are presented in Table 2. Although the climate in Hong Kong is markedly seasonal with a clearly defined wet season, it is found that the concentration of COD and NH₃-N in the raw leachate samples, which were collected in December 2004 (winter) as well as July 2005 (summer and rainy season), did not show any significant seasonal variations. This fact was different from another study in Thailand [3], which found that the concentration of organic material in the leachate was very much higher in dry season than that in rainy season, since the leachate was diluted with rainwater. This particular phenomenon suggests that the physico-chemical characteristics of the leachate from the NENT landfill were not significantly affected by rainfall conditions and that both saturated and unsaturated solid waste in the landfill had the ability to buffer short-term variation, as indicated by the relatively stable short-term quality and quantity of the leachate. These two characteristics confirm similar findings in the other studies undertaken in Hong Kong [21] and Taiwan [28], which reported that there were no significant seasonal variations in the quality and the quantity of leachate between dry and rainy seasons. This indicates that the influence of seasonal variations in the quantity and quality of landfill leachate varies from one region to another, depending on the seasonal climate and the hydrology site of the landfill [29].

It is also found that the leachate sample has a biodegradability ratio (BOD₅/COD) of 0.09, typical of raw leachate from the methanogenic phase [30]. The result suggests that most of the organic materials in the leachate have been converted to methane, thus decreasing the ratio of the biodegradability of the leachate. The low biodegradability ratio also indicates that the leachate was from a stabilized landfill, which can be better

Table 2
Physico-chemical properties of raw leachate from the NENT landfill (Hong Kong)

	December 2004 (winter)	July 2005 (rainy and summer)	Temporal fluctuation (%)
pH	8.01	7.81	2.50
COD (mg/L)	8000	7622	4.72
BOD ₅ (mg/L)	700	565	19.28
BOD ₅ /COD	0.09	0.07	22.22
NH ₃ -N (mg/L)	2620	2390	8.78
NO ₃ -N (mg/L)	21	18	14.28
Total Kjeldahl nitrogen (mg/L)	2851	2590	9.15
Na ⁺ (mg/L)	1505	1222	18.80
K ⁺ (mg/L)	1082	871	19.50
Mg ²⁺ (mg/L)	25	22	12.00
Ca ²⁺ (mg/L)	23	18	21.74
Alkalinity (mg/L)	12986	11668	10.15
TOC (mg/L)	2590	2316	10.58
Electrical conductivity (mS/cm)	12.53	9.99	20.27

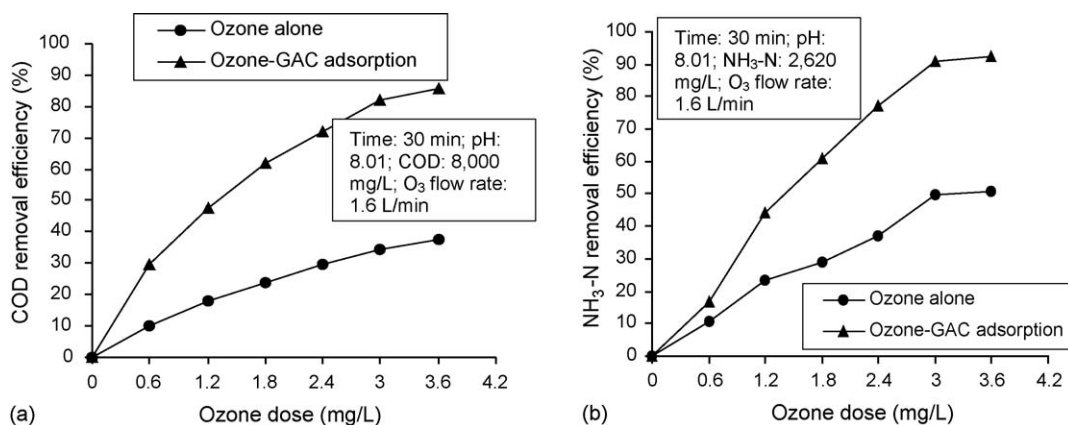


Fig. 2. Effects of ozone dose on the removal of COD (a) and NH₃-N (b) from landfill leachate.

treated with physico-chemical treatment techniques than with biological process.

In addition to organic compounds, the leachate from the NENT landfill also contained inorganic substances such as heavy metals, as indicated by the conductivity value. Due to competition with heavy metals for adsorption sites, the existence of such impurities in the leachate might lower the adsorption capacities of the adsorbent for organic compounds.

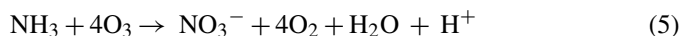
3.2. Effects of ozone dose on the removal of COD and/or NH₃-N

In the oxidation process, the removal efficiency of COD/NH₃-N varies with the dose of oxidant. Therefore, a study determining the optimum dose of ozone was conducted to achieve a maximum removal of COD/NH₃-N during equilibrium conditions. Fig. 2 presents the effects of ozone dose on the removal efficiency of COD and NH₃-N after ozonation alone and/or combined ozone-GAC adsorption.

After ozonation alone, it is found that the COD removal improved from 10% to 35% at an initial COD concentration of 8000 mg/L with an increasing ozone dose from 0.6 to 3 mg/L, which leveled after 3 mg/L of ozone dose. This could be stemmed from the fact that as the ozone oxidation continued, recalcitrant organic compounds in the leachate that could be oxidized became less available and that the remaining organic compounds after ozone oxidation were difficult to break down. Since stabilized leachate mostly contains humic substances that are less prone to ozonation and the substances are more aliphatic and less aromatic [31], there was no significant increase in the COD removal after applying a certain ozone dose.

It is also found that the combination of ozone treatment followed by GAC adsorption significantly improved the COD removal from 29% to 86%, compared to ozonation alone (35%) at the same COD concentration of 8000 mg/L ($p \leq 0.05$, paired t -test). The local regulation for the protection of groundwater from pollution by landfill leaching requires that the treated leachate should contain less than 200 mg/L of COD. It is found that the integrated ozone-GAC adsorption treatment could not generate an effluent that complied with the local regulation.

Similarly, the NH₃-N removal significantly improved from 17% to 92% when the ozone dose increased from 0.6 to 3.0 mg/L ($p \leq 0.05$, paired t -test). In this case, ammonia could be removed by ozone through the advanced oxidation process (AOP), in which •OH radicals with an oxidation potential of 2.80 V, resulting from the ozone decomposition at pH ranging from 8 to 9, played a major role throughout the oxidative treatment. During the ozone oxidation, the toxic ammonia was converted to relatively harmless nitrate, as shown in the following reaction [32]:



After ozonation with 3 mg/L of dose, the concentration of NO₃⁻ (represented by NO₃⁻-N) in the leachate increased 42% from 21 to 30 mg/L. Similarly, the concentration of H⁺ ions in the leachate also increased, as reflected by a decreasing pH value from 8.01 (initial conditions) to 7.14 (after ozonation). Wang and Pai [33] reported that ammonia is slowly oxidized by the ozone, as indicated by the low kinetic rate of the oxidation reaction. For this reason, the extent of NH₃-N removal after ozone treatment is rarely reported.

It is important to note that the integrated treatment process was still unable to achieve the NH₃-N discharge standard of less than 0.02 mg/L, the concentration recommended by the US EPA to prevent fish toxicity [34]. This result suggests that further biological treatments such as activated sludge or nitrification to complement the biodegradation of the leachate are still required to comply with the environmental legislation.

3.3. Effects of initial pH on the removal of COD and/or NH₃-N

It is widely known that pH plays a major role in the decomposition of ozone in solution. In alkaline conditions (pH > 8), once the reaction of free radical was initiated by the ozone, a series of oxidative degradation reactions that completely oxidized the recalcitrant organic materials into CO₂ and H₂O occurred in the solution. Therefore, the effects of pH on the treatment performance of ozonation alone and/or combined ozone-GAC adsorption treatment were studied by varying pH from 3 to 9, while

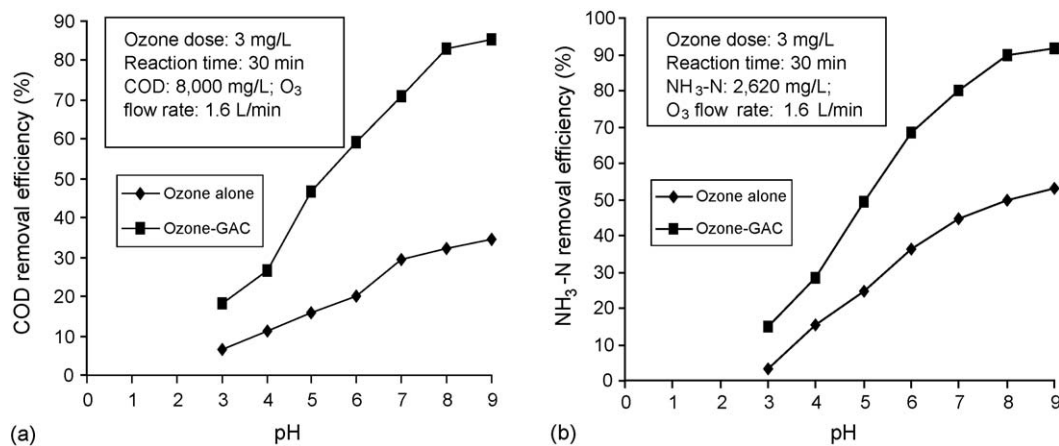


Fig. 3. Effects of pH on the removal of COD (a) and $\text{NH}_3\text{-N}$ (b) from landfill leachate.

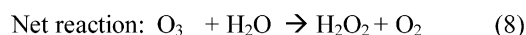
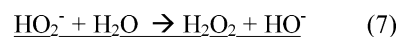
keeping other parameters such as ozone dose and reaction time as constant. Fig. 3 depicts the effects of initial pH on the removal of COD and/or $\text{NH}_3\text{-N}$ from landfill leachate.

It is observed from Fig. 3 that after ozone-GAC adsorption treatment, the COD removal significantly improved from 18% to 86% with an increasing pH in an alkaline environment (pH 8–9), compared to that of ozonation alone (35%) at the same initial COD concentration of 8000 mg/L ($p \leq 0.05$, paired t -test). This could be attributed to the fact that in alkaline conditions, the concentrations of OH^- in the solution significantly increased. With the increasing OH^- in the solution that initiated the intermediate chain reactions, the rate of ozone decomposition also became significantly faster. The ozone attacked the polar bonds of GAC, causing bond breaking, thus leading to the direct formation of $\bullet\text{OH}$ radicals as an oxidant. The radicals formed were not bound to the surface of GAC, but free to react in the aqueous phase. In this process, the delocalized π electron system in the basic group of GAC and the oxygenated basic groups (chromene and pyrone) acting as the Lewis bases might play a major role as the catalytic centers of reactions, reducing the ozone molecules to OH^- and H_2O_2 [35].

In their study, Sanchez-Polo et al. [35] also confirmed that ozonation in the presence of GAC could oxidize the recalcitrant organic pollutants in the solution either by a direct reaction of the compounds with the ozone or by $\bullet\text{OH}$ radicals that were produced in the interaction between the ozone and the surface of GAC, which contained some functional groups such as carboxylic, hydroxyl and lactone [36]. In an alkaline environment (pH 8–10), OH^- ions acted as the promoter/initiator for the decomposition of ozone into intermediate compounds such as peroxide ions (O_2^-) and the $\text{HO}_2\bullet$ radicals that were also reactive [37,38]. In this case, through the dispersive interactions between π electrons of the aromatic rings and those of the carbon basal plane (graphenic layer), the surface properties and the textural characteristics of the GAC played an important role in transforming ozone into $\bullet\text{OH}$ radicals [35].

In alkaline conditions, the OH^- ions also facilitated the formation of $\bullet\text{OH}$ through an indirect route. The OH^- ions reacted with ozone to form hydroperoxide ion (HO_2^-), which was the conjugate base of H_2O_2 [39] (Eq. (6)). At a pH lower than 11.6

(the pK_a of H_2O_2), HO_2^- would be converted to H_2O_2 (Eq. (7)). Therefore, the increasing concentration of OH^- ions also facilitated the formation of H_2O_2 , which was a source of $\bullet\text{OH}$ radicals. The overall process is presented in Eq. (8) as a net reaction:



The case was similar for $\text{NH}_3\text{-N}$ removal. The combination of ozone and GAC adsorption gave a significantly higher $\text{NH}_3\text{-N}$ removal (92%) than ozonation alone (50%) at the same initial $\text{NH}_3\text{-N}$ concentration of 2620 mg/L ($p \leq 0.05$, paired t -test). Such a phenomenon might be attributed to the fact that GAC played a major role in the overall degradation process through (a) the adsorption of the contaminant on the surface of GAC; (b) the promotion of the ozone decomposition via the generation of $\bullet\text{OH}$ radicals in the solution. The $\bullet\text{OH}$ radicals had a greater oxidizing capacity (2.80 V) than ozone (2.08 V). As a result, either by hydrogen abstraction or by electrophilic attack to double bonds, the $\bullet\text{OH}$ radicals-catalyzed ozone not only reacted with $\text{NH}_3\text{-N}$, but also broke down other large compounds such as xenobiotic compounds, adsorptive organic halogen (AOX) and phenolic compounds in the leachate into oxidation by-products that had a smaller molecular size than the starting compounds [40]. Consequently, the by-products became more easily biodegradable, thus enabling GAC to adsorb the remaining organic materials unchanged by the ozone oxidation.

3.4. Effects of individual and/or combined treatments on the biodegradability of leachate

Fig. 4 presents the relationship between the ratio of BOD_5/COD and the reaction time required for the degradation of the leachate. As reflected by the biodegradability ratio, it was found that the biodegradability of landfill leachate improved significantly from 0.09 to 0.47 after ozone-GAC adsorption treatment ($p \leq 0.05$, ANOVA test), suggesting that more organic

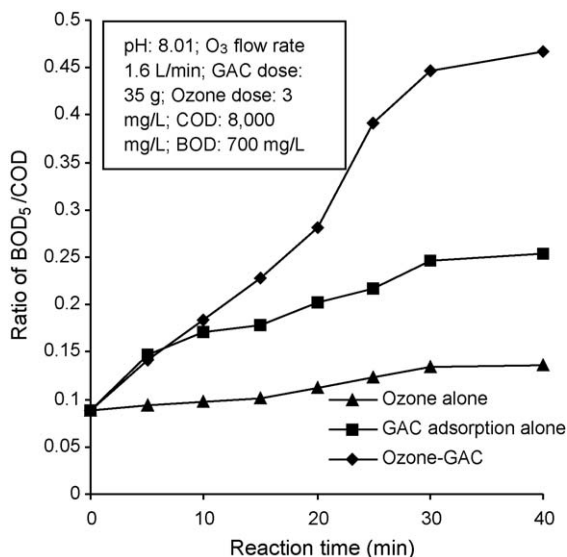


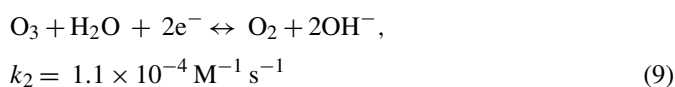
Fig. 4. Effects of various treatments on the biodegradability of landfill leachate.

compounds in the leachate were degraded into smaller molecules [41].

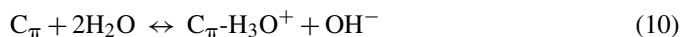
Of the three treatments investigated, the combination of ozone-GAC adsorption has the highest biodegradability ratio of the leachate (0.47), compared to the other two individual treatments alone (ozonation: 0.14; GAC adsorption: 0.25) ($p \leq 0.05$, Tukey's HSD test). The improving BOD/COD ratio by ozonation after the addition of GAC might be due to the fact that the surface of GAC promoted the ozone oxidation that subsequently destroyed large organic compounds through the formation of $\bullet\text{OH}$ radicals that initiated the radical-type chain reactions of ozone decomposition in the solution [42]. In this case, the ozone might attack the pyrrolic groups of the graphenic layers in GAC (basal plane electron) that acted as Lewis bases to generate N -oxide-type groups and hydroperoxide radical ($\text{HO}_2\bullet$). The generation of $\text{HO}_2\bullet$ radicals was reported to improve the kinetic rate of ozone decomposition into $\bullet\text{OH}$ radicals [43].

In the pyrrol group, the pair of nitrogen lone electrons formed part of the electronic cloud of the aromatic ring. As a result, the presence of pyrrol groups on the surface of GAC improved the electronic density on its basal plane, thus enhancing the concentration of $\bullet\text{O}_2^-$ (superoxide radical) in the system [43]. The transfer of an electron from $\bullet\text{O}_2^-$ radicals to O_3 molecule resulted in the formation of $\bullet\text{O}_3^-$ (ozonide radical) as an intermediate and subsequently led to the generation of $\bullet\text{OH}$ radicals [44]. In the solution, $\bullet\text{OH}$ radicals rapidly reacted ($k = 10^8$ to $10^{11} \text{ M}^{-1} \text{ s}^{-1}$) with most of the target organic compounds in the liquid phase [45].

There are some steps for the formation of $\bullet\text{OH}$ radicals, resulting from GAC catalytic ozonation. In the solution, the reduction of ozone on the surface of GAC was reported to generate OH^- ions (Eq. (9)) [43]:



Due to its electrophilic properties, ozone might have a higher affinity towards the basic Lewis in the surface of GAC sites, specifically on aromatic compounds, which are π electron-rich regions. For the aromatics substituted with electron donor groups such as $-\text{OH}$, the initial attack of the ozone occurred at an *ortho*- and *para*-position [46], resulting in the ozone decomposition into $\bullet\text{OH}$ radicals. The increase in the π -electron system of GAC due to the pyrrol groups also increased the physico-chemical interaction between GAC and the water molecules to form OH^- ions (Eq. (10)) [45]:

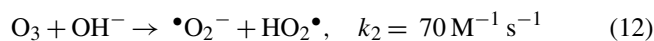


Combination of the two equations (9) and (10) gives the overall reaction of GAC catalytic ozonation as follows:

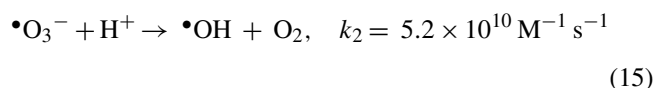
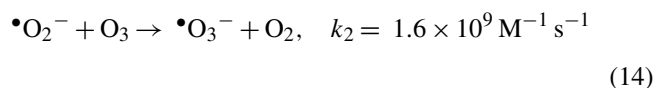
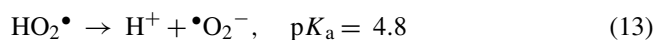


Eq. (11) suggests that the number of OH^- ions in the solution increased for combined ozone-GAC adsorption treatments, compared to that of individual ozonation or GAC alone. Since both the OH^- ions and $\bullet\text{OH}$ radicals have a proportional ratio of mole as indicated by the ratio of their reaction coefficients (Eq. (12)), the number of OH^- ions produced in Eq. (11) also represents the amount of $\bullet\text{OH}$ radicals that would be generated in Eq. (15). Such a phenomenon indicates the synergistic effects between the two physico-chemical treatments in the formation of $\bullet\text{OH}$ radicals. As the solution pH increased to 9 or the concentration of H^+ ions decreased (to 10^{-9} M), the reaction equilibrium shifted from left to right, resulting in the production of more OH^- ions in the solution, thus leading to the generation of more $\bullet\text{OH}$ radicals (Eqs. (12)–(15)). In this case, the OH^- ions facilitated the formation of $\bullet\text{OH}$ radicals through its reaction with ozone as reported elsewhere [47]:

- Initial reaction:



- Propagation:

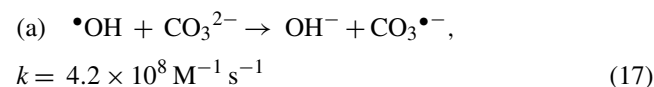


- Termination:



where P represents the scavenger of hydroxyl radicals such as HCO_3^- and CO_3^{2-} .

Some examples of the reaction are presented as follows:



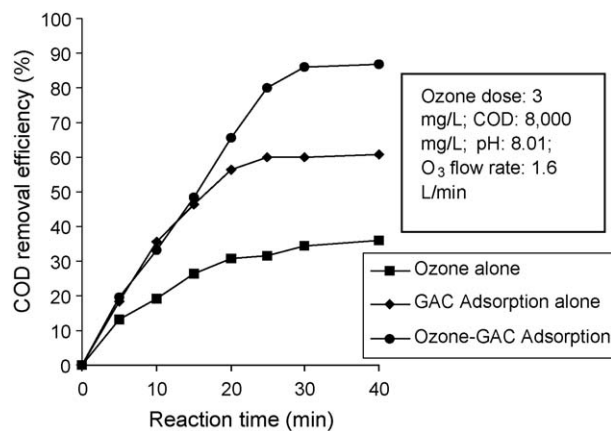
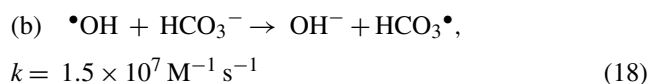


Fig. 5. Comparison of COD removal among different types of treatment.



As seen from Eq. (16), $\bullet\text{OH}$ radicals are the responsible species for GAC catalytic ozonation. For this reason, it is suggested that ozone/GAC is a kind of advanced oxidation process (AOP) controlled by a free radical mechanism, in which GAC functions as the initiator that enhances the transformation of the ozone into $\bullet\text{OH}$ radicals [48,49]. Therefore, the combination of ozone-GAC adsorption has significantly better treatment performance than ozonation alone in degrading recalcitrant compounds in the leachate.

3.5. Removal mechanisms of recalcitrant compounds from leachate by ozone-GAC adsorption

To study the extent of the role of GAC in the removal of organic compounds from the leachate by the combined ozone-GAC adsorption treatment, the removal efficiency of COD is presented as a function of reaction time.

It can be observed from Fig. 5 that within the first 10 min, GAC adsorption controlled the removal of organic compounds from the leachate. Between 10 and 15 min, both GAC adsorption and ozonation played equally important roles in the oxidation, since GAC served both as an adsorbent and a promoter [50]. As an adsorbent, GAC adsorbed the organic matter from the leachate on its surface, while as a promoter, it initiated the ozone

decomposition into $\bullet\text{OH}$ radicals. In this case, GAC acted as the initiator of the radical-type chain reactions that transformed ozone into $\bullet\text{OH}$ in the aqueous phase.

After a short period of ozonation, the degradation of the recalcitrant organics in the leachate by GAC took place. This was evident from the change of leachate color from brown (initial conditions) due to the presence of humic substances to light yellow (after ozonation). The reduction of color intensity clearly indicated that there was a direct attack of ozone on the double bonds of GAC (in the chromophoric parts) during the ozone treatment [51]. After ozonation had decomposed the recalcitrant compounds into smaller molecules, the organic materials in the leachate became more easily biodegradable, enabling GAC to easily adsorb the remaining organic materials unchanged during the ozonation [52]. This is one of the advantages of using this combined treatment for the removal of refractory compounds from stabilized leachate.

After 20 min, GAC became saturated, as there was no further increase in the COD removal. During the last 25 min, under alkaline conditions ($\text{pH} > 7$), ozonation became the primary factor that controlled the removal of organic compounds from the leachate. In this case, the nature of the compounds present in the leachate would determine the degree of reactivity with the ozone. Compounds with specific functional groups such as the aromatic ring or double bonds were prone to ozone attack [53,54]. In alkaline conditions, the indirect oxidation mechanism involved the reactions between the organic compounds and the formed $\bullet\text{OH}$ radicals and resulted in the degradation of recalcitrant contaminants in the leachate.

Although GAC adsorption was more effective than ozonation alone in terms of COD removal, the combination of these two methods into an integrated process was found to be a more attractive option for the treatment of stabilized leachate, since it offered synergistic effects on the removal of many recalcitrant compounds such as xenobiotic and AOX compounds [55]. Ozone oxidation could rapidly react with most of the recalcitrant organic compounds in the leachate, breaking them down into smaller and more biodegradable ones, thus enabling the subsequently easier adsorption of the more oxidized by-products by GAC. This was indicated by the increasing number of the bed volume (BV) of the leachate that could be treated by ozone-treated GAC during the column operation (Table 3). In addition, the spent GAC could be restored after becoming completely saturated through regeneration by using ozone at least three times for subsequent use before becoming completely useless, thus improving the cost-effectiveness of this combined method.

Table 3
Column performance of GAC for COD and/or $\text{NH}_3\text{-N}$

Type of adsorbent	COD removal			$\text{NH}_3\text{-N}$ removal		
	Number of BV at breakthrough point	Number of BV at saturation point	Adsorption capacity (mg/g)	Number of BV at breakthrough point	Number of BV at saturation point	Adsorption capacity (mg/g)
Ozone-treated GAC	4	18	259.34	2	14	99.86
As-received GAC	1	9	165.46	0.5	8	53.58

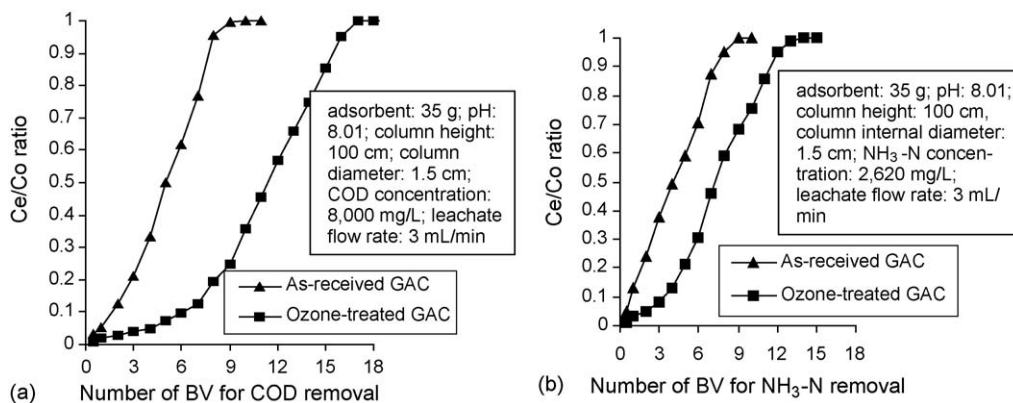


Fig. 6. Breakthrough curves of all types of GAC on the removal of COD (a) and NH_3-N (b) for the first run.

3.6. Effects of surface modification of GAC with ozone on the removal of COD and/or NH_3-N

In this study, the effects of surface modification of GAC with ozone on the removal efficiency of COD and NH_3-N were investigated using column studies. Fig. 6 presents the breakthrough curves of both types of adsorbents (as-received GAC and ozone-modified GAC) on COD and/or NH_3-N removal. It is important to note that the breakthrough point is achieved when the residual organic compounds or NH_3-N first appear in the effluent ($C_e/C_0 = 0.05$), while the number of bed volumes (BV) is defined as the ratio between the volume of leachate treated and the volume of GAC used in the column [56].

It is observed from Fig. 6 that the complete breakthrough curves of the two types of GAC for the first run on COD and NH_3-N removal are of the traditional "S" shape. It is important to note that one run is defined as one loading step of organic compounds. Table 3 presents the breakthrough and saturation points of ozone-treated GAC and as-received GAC for COD and NH_3-N removal.

Table 3 indicates that ozone-treated GAC achieved a significantly longer breakthrough point (BV: 4) with more leachate that could be treated (0.735 L) than as-received GAC (BV: 1; 0.105 L) for COD removal ($p \leq 0.05$, paired *t*-test). About 10.7 L of leachate (18 BV) passed through the column before it became completely exhausted for the first run of ozone-treated GAC, while as-received GAC could treat only 3.2 L of leachate (9 BV) prior to the saturation point ($C_e/C_0 = 1$).

The trends of breakthrough and saturation points for NH_3-N removal are also similar. As-received GAC achieved a significantly earlier breakthrough point (BV: 0.5; 0.035 L) than ozone-treated GAC (BV: 2; 0.245 L) for the first run ($p \leq 0.05$, paired *t*-test). About 6.4 L of leachate (14 BV) passed through the column before the ozone-treated GAC inside the column was completely exhausted, while as-received GAC could treat only 2.6 L of leachate (8 BV) before complete saturation.

To describe the adsorption kinetics, the Loebensteinin model was employed using the data obtained for COD during the col-

umn experiments [27], as shown in the following equation:

$$\log \left(\frac{C_0}{C-1} \right) = \frac{kXW}{R} - \frac{kC_0V}{R} \quad (19)$$

If C_0 and R are considered to be constant, the plot of $\log(C_0/(C-1))$ versus V should give a straight line with a slope equal to $-kC_0/R$ and with kXW/R as the intercept. The value of k (rate coefficient) and X (the adsorption capacity of adsorbent at saturation level) were determined from the slope and intercept values obtained from the plot, respectively.

As shown in Table 3, ozone-treated GAC gave significantly higher adsorption capacities of COD and NH_3-N in column operation than as-received GAC. Such different phenomena between the two types of GAC could be explained by the fact that the oxidative treatment of GAC with ozone generated more adsorption sites and oxygen functional groups on its surface [57,58]. Consequently, the ozone-oxidized GAC required a longer time to achieve the breakthrough/saturation points, resulting in a larger number of bed volume that could be treated by the adsorbent.

In addition, the prolonged exposure of GAC to ozone modified the chemical composition of the surface of GAC. After ozone treatment, the basic sites were transformed into acid ones. Carbonyl- and carboxyl-type oxygenated functional groups that predominated on the surface of GAC were the main causes of the development of the negative surface charge on GAC [52]. In this case, ozone treatment on the surface of GAC might increase its polarity, thereby enhancing its electrostatic interactions with the positive charge of organic contaminants in the solution for a higher removal [58,59].

It is interesting to note that the results of the adsorption capacity in the column studies were higher than those obtained in batch studies carried out also by us [60], in which the adsorption capacities of ozone-treated GAC were 243.43 and 87.36 mg/g for COD and NH_3-N , respectively. This phenomenon might be attributed to the inherent difference in the nature of the two studies. In the batch experiments, the concentration gradient decreased with increasing contact time; while in the column operation, the adsorbent had continuous physico-chemical contact with fresh feeding solution at the interface of the adsorption zone, as the adsorbate solution passed through the column. Consequently,

Table 4
Comparison of the removal of COD and/or NH₃-N from landfill leachate using various treatments

Type of treatment	Type of precipitant/ adsorbent/ membrane	Dose (g/L)	Initial concentration in the leachate (mg/L)		Pressure (bar)	BOD/ COD	pH	Removal efficiency/ rejection rate (%)		Reference
			COD	NH ₃ -N				COD	NH ₃ -N	
Individual treatment										
Ammonia stripping	Ca(OH) ₂	11	5850	3260	–	0.60	11.0	–	94	[61]
Precipitation	Struvite	NA	7511	5618	–	0.22	8.5–9.0	–	98	[7]
RO	SW30-2521	–	3840	NA	52	0.31	6.0	98	NA	[62]
NF	NA	NA	17000	3350	NA	0.03	6.4	96	NA	[63]
Adsorption	PAC	6	5690	2215	–	NA	NA	95	NA	[30]
Ozonation	O ₃	3.6	1090	455	–	0.04	8.3	70	67	[64]
Ozonation	O ₃	3 × 10 ⁻³	8000	2620	–	0.09	8	35	50	Present study
Combined treatments										
RO + UASB	–	–	35000	1600	NA	–	7.4	99	99	[65]
RO + activated sludge	–	–	6440	1153	NA	0.70	NA	99	99	[66]
RO + evaporation	AD	–	19900	30	60	0.20	6.4	88	97	[67]
NF + adsorption + ozonation	Desal 5 K	–	4000	NA	8.5	NA	6.5	99	NA	[68]
	GAC	NA								
	O ₃	NA								
UF + adsorption	GAC	NA	3050	NA	–	0.55	7.0	97	NA	[69]
Fenton oxidation + adsorption	Fe(II)	0.8	2020	3400	–	0.13	4.0	92	NA	[70]
	H ₂ O ₂	0.5								
	PAC	0.5								
Coagulation + Fenton oxidation	FeCl ₃	5 × 10 ⁻¹	7400	NA	–	0.06	8.5	90	NA	[41]
	Fe(II) H ₂ O ₂	NA								
Ozonation + adsorption	O ₃	5 × 10 ⁻²	4970	700	–	0.17	8–9	90	NA	[25]
	GAC	5								
Ozonation + adsorption	O ₃ GAC	3 × 10 ⁻³	8000	2620	–	0.09	8	86	92	Present study

Remarks—NA: not available.

the removal of organic compounds by ozone-treated GAC in the column studies was higher than that of the batch studies.

3.7. Comparison of treatment performance between combined ozone-GAC adsorption and other physico-chemical techniques for landfill leachate

To evaluate the performances of different treatments investigated in the present study, a comparative study is made in terms of the pH, dose required (g/L), and initial concentration ranges of COD and NH₃-N (mg/L) in the landfill leachate. Although it only has a relative meaning due to the different testing conditions such as pH, temperature, the strength of wastewater, seasonal climate, and hydrology site, this comparison is still useful to evaluate the overall treatment performance of each technique. Table 4 summarizes the removal performance of various individual and/or combined treatments on COD and/or NH₃-N in other studies.

Table 4 shows that struvite precipitation achieved 98% of treatment efficiency for NH₃-N removal with an initial concentration of 7511 mg/L. An outstanding (96–98%) COD removal was also demonstrated by nanofiltration (NF) and reverse osmosis (RO) with the COD concentrations ranging from 3840 to

17,000 mg/L. Among the combined treatments surveyed from the literature, the combination of RO and an upflow anaerobic sludge blanket (UASB) (with initial COD and NH₃-N concentrations of 35,000 and 1600 mg/L, respectively) and/or RO and activated sludge (COD: 6440 mg/L; NH₃-N: 1153 mg/L) achieved an almost complete removal of COD and NH₃-N. When compared to the treatment efficiencies presented in Table 4, the removal of COD (86%) and/or NH₃-N (92%) by a combination of ozone-GAC treatment in the current study was relatively satisfactory. In fact, for the same type of combined treatments, the total COD removal in this study was higher (86% out of 8000 mg/L) than that of another study conducted by Rivas et al. [25], who had a 90% of COD removal with an initial concentration of 4970 mg/L (Table 4).

3.8. Comparison of cost-effectiveness between combined ozone-GAC adsorption and other physico-chemical techniques for landfill leachate

Basically, the treatment costs of landfill leachate vary, depending on its strength and quantity, the process employed, the local condition of a landfill site, the amount and composition of impurities, as well as the extent of purification [71,72]. The

overall treatment cost includes the construction as well as operational and maintenance costs (O&M). The construction costs normally depend on the effluent quality required and the capacity of the installation, while O&M costs cover manpower, energy, chemicals and maintenance. The manpower cost significantly varies from one region/country to another.

In this study, the treatment cost of leachate using combined ozone-GAC adsorption treatment is estimated to vary between US\$ 2 and 4 m^{-3} of treated effluent. The cost mainly covers the chemicals required and energy consumption, but it does not take into account any costs associated with the regeneration of the adsorbent or other operational costs such as labor, transportation for leachate collection and maintenance. The cost-effectiveness of using this combined treatment can be improved if the spent GAC can be chemically regenerated for multiple uses, without altering its removal performance for organic compounds and/or $\text{NH}_3\text{-N}$. To obtain an accurate assessment of the operational cost for leachate treatment, a pilot study needs to be carried out [73].

It is important to note that the operational cost of leachate treatment varies from time to time, as both the quality and the quantity of the leachate would change due to seasonal weather variations. To cope with the problems of temporal fluctuations in the quantity and composition of the leachate, the treatment facilities would need an extensive upgrading, thus resulting in an increase in the operational cost. In addition, it is difficult to estimate a reliable treatment cost for landfill leachate due to the many cost components that are involved such as the collection system, treatment facility and handling. Therefore, information on the treatment cost of landfill leachate is rarely reported.

In spite of these, some researchers have estimated the overall treatment cost of leachate using certain treatment methods. Li et al. [7] reported that the treatment cost for $\text{NH}_3\text{-N}$ removal using struvite precipitation was one-fifth more expensive than that of ammonium stripping. Depending on the type of precipitation and chemicals employed, the treatment cost of struvite precipitation varies between US\$ 2 and 4 m^{-3} of treated effluent [74].

Subject to the size and complexity of the RO plant, the overall treatment cost of landfill leachate in Germany is in the range of US\$ $2\text{--}30\text{ m}^{-3}$ [75,76]. A combination of biological and physico-chemical treatments that could meet the German requirements cost about US\$ 41 m^{-3} [77]. The cost could be reduced if the RO systems were supplied with a storage lagoon that could level off the seasonal variations during the production of leachate.

When compared to RO, the treatment cost using evaporation and thermal oxidation was more expensive, ranging from US\$ 30 to 70 m^{-3} [78]. The evaporation of leachate using plastic film as a heat exchanger was reported to be US\$ 4 m^{-3} [79]. Depending on the liner, pump and land costs, it is estimated that the treatment cost for constructed wetlands in the USA is about US\$ $50,000\text{ ha}^{-1}\text{ year}^{-1}$ [80]. Liners and land acquisition, pumps and piping are included as the basic costs of excavation and vegetation establishment. For large systems, a wetland requires O&M cost of US\$ $990\text{ ha}^{-1}\text{ year}^{-1}$ [81].

Although many treatment techniques can be employed to remove recalcitrant compounds from landfill leachate, the most important aspect in the selection of leachate treatment method

is that an appropriate and cost-effective solution be adopted. This means that the treated effluent can meet the local discharge standards for COD and $\text{NH}_3\text{-N}$ at a low cost. In addition, the selected treatment should be flexible enough to remain useful with changing technology, regulation, leachate characteristics and economic factors. All these factors should be taken into consideration when selecting the most effective and inexpensive treatment technology in order to protect the environment.

4. Conclusions

It is evident from the study that the use of ozone-GAC adsorption for COD and/or $\text{NH}_3\text{-N}$ removal is technically applicable and attractive. The advantages of using this combination for leachate treatment are the simplicity of the system and its ability to accept a varying strength and composition of landfill leachate with seasonal variations.

Among the treatments studied, the combination of ozone-GAC adsorption using ozone-modified GAC had the highest removal performance for COD (86%) and/or $\text{NH}_3\text{-N}$ (92%) when compared to ozonation alone (COD: 35%; $\text{NH}_3\text{-N}$: 50%) at the same initial COD and/or $\text{NH}_3\text{-N}$ concentrations of 8000 and 2620 mg/L, respectively. Although the integrated treatment was more effective than ozonation alone for treating stabilized leachate, the results suggested that it could not generate treated effluent that complied with the COD limit of lower than 200 mg/L and the $\text{NH}_3\text{-N}$ discharge standard of less than 5 mg/L. Therefore, further biological treatments such as activated sludge or nitrification are still required not only to complement the degradation of the leachate, but also to comply with the environmental legislation.

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References

- [1] M. El-Fadel, A.N. Findikakis, J.O. Leckie, Environmental impacts of solid waste landfilling, *J. Environ. Manage.* 50 (1997) 1–25.
- [2] K. Westlake, *Landfill Waste Pollution and Control*, Albion Publishing, Sussex, 1995.
- [3] S. Babel, Laboratory Scale Studies for Treatment of Solid Waste Landfill Leachate Using Crossflow Microfiltration and Ozone, PhD Thesis, Asian Institute of Technology, Pathumthani, 1993.
- [4] US Environmental Protection Agency (EPA), *Municipal Solid Waste in the United States: 2000 Facts and Figures*, Office of Solid Waste and Emergency Response, Washington DC, 2002 (EPA 530-R-02-001).
- [5] Z.Y. Feng, D. Na, L.J. Hong, X.C. Zhong, A new pyrolysis technology and equipment for treatment of municipal household garbage and hospital waste, *Renew. Energy* 28 (15) (2003) 2383–2993.

- [6] US EPA, Urban watershed management research terminology, 2005. <http://www.epa.gov/ednrmrl/terminology.htm#L>.
- [7] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, *Waste Manage.* 19 (1999) 409–415.
- [8] X.Z. Li, Q.L. Zhao, MAP precipitation from landfill leachate and seawater bitter waste, *Environ. Technol.* 23 (9) (2002) 989–1000.
- [9] W.R. Ernst, P. Hennigar, K. Doe, S. Wade, G. Julien, Characterization of the chemical constituents and toxicity to aquatic organisms of a municipal landfill leachate, *Water Pollut. Res. J. Can.* 29 (1994) 89–101.
- [10] A. Baun, L. Kløft, P.L. Bjerbg, N. Nyholm, Toxicity testing of organic chemicals in groundwater polluted with landfill leachate, *Environ. Toxicol. Chem.* 18 (1999) 2046–2053.
- [11] S.Q. Burton, I.A. Watson-Craik, Ammonia and nitrogen fluxes in landfill sites: applicability to sustainable landfilling, *Waste Manage. Res.* 16 (1998) 41–53.
- [12] A.C. Silva, M. Dezotti, G.L. Sant'Anna Jr., Treatment and detoxification of a sanitary landfill leachate, *Chemosphere* 55 (2004) 207–214.
- [13] T. Assmuth, S. Penttilae, Characteristics, determinants and interpretation of acute lethality in daphnids exposed to complex waste leachates, *Aquat. Toxicol.* 31 (1995) 125–141.
- [14] M. Nohava, W.R. Vogel, H. Gaugitsch, Evaluation of the luminescent bacteria bioassay for the estimation of the toxicological potential of effluent water samples—comparison with data from chemical analysis, *Environ. Int.* 21 (1995) 33–37.
- [15] A. Bagchi, Design Construction and Monitoring of Landfills, John Wiley & Sons, New York, 1994.
- [16] X.Z. Li, Q.L. Zhao, Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer, *Ecol. Eng.* 20 (2003) 171–181.
- [17] A. Al-Kdasi, A. Idris, K. Saed, C.T. Guan, Treatment of textile wastewater by advanced oxidation processes—a review, *Global Nest: The Int. J.* 6 (3) (2004) 226–234.
- [18] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation process, *Chemosphere* 54 (7) (2004) 997–1003.
- [19] J. Fettig, H. Stapel, C. Steinert, M. Geiger, Treatment of landfill leachate by pre-ozonation and adsorption in activated carbon columns, *Water Sci. Technol.* 34 (9) (1996) 33–40.
- [20] K. Ikehata, M.G. El-Din, Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation processes: a review, *Ozone: Sci. Eng.* 26 (2004) 327–343.
- [21] I.M.C. Lo, Characteristics and treatment of leachates from domestic landfills, *Environ. Int.* 22 (4) (1996) 433–442.
- [22] C.T.T. Chan, A Pilot Study on Testing of Full Denitrification in Existing Leachate Treatment Works of Northeast New Territories (NENT) Landfill, MPhil Thesis, The Hong Kong Polytechnic University, Hong Kong, 1999.
- [23] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association (APHA), Washington, 1998.
- [24] H.L. Chiang, C.P. Huang, P.C. Chiang, The surface characteristics of activated carbon as affected by ozone and alkaline treatment, *Chemosphere* 47 (2002) 257–265.
- [25] F.J. Rivas, F. Beltrán, O. Gimeno, B. Acedo, F. Carvalho, Stabilized leachates: ozone-activated carbon treatment and kinetics, *Water Res.* 37 (2003) 4823–4834.
- [26] M. Elovitz, U. Gunten, Hydroxyl radical/ozone ratios during ozonation processes. I. The reaction concept, *Ozone: Sci. Eng.* 21 (3) (1999) 239–260.
- [27] B. Morawe, D.S. Ramteke, A. Vogelpohl, Activated carbon column performance studies of biologically treated landfill leachate, *Chem. Eng. Proc.* 34 (1995) 299–303.
- [28] H.J. Fan, H.Y. Shu, H.S. Yang, W.C. Chen, Characteristics of landfill leachate in Central Taiwan, *Sci. Total Environ.*, in press.
- [29] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, *J. Hazard. Mater.* 129 (1–3) (2006) 80–100.
- [30] E. Diamadopoulos, Characterization and treatment of recirculation-stabilized leachate, *Water Res.* 28 (1994) 2439–2445.
- [31] F. Wang, M.G. El-Din, D.W. Smith, Oxidation of aged raw landfill leachate with O₃ only and O₃/H₂O₂: treatment efficiency and molecular size distribution analysis, *Ozone: Sci. Eng.* 26 (2004) 287–298.
- [32] W.R. Haag, J. Hoigné, H. Bader, Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment, *Water Res.* 18 (9) (1984) 1125–1128.
- [33] G.S. Wang, S.Y. Pai, Ozonation of dissolved organic matter in biologically treated wastewater effluents, *Ozone: Sci. Eng.* 23 (5) (2001) 351–358.
- [34] K.C. Cheung, L.M. Chu, M.H. Wong, Ammonia stripping as a pretreatment for landfill leachate, *Water Air Soil Pollut.* 94 (1997) 209–221.
- [35] M. Sanchez-Polo, U. Gunten, J. Rivera-Utrilla, Efficiency of activated carbon to transform ozone into •OH radicals: influence of operational parameters, *Water Res.* 39 (2005) 3189–3198.
- [36] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium(VI) from solution by coconut husk and palm pressed fibers, *Environ. Technol.* 14 (1993) 277–282.
- [37] Y. Takeuchi, K. Mochizuki, N. Matsunobu, R. Kojima, H. Motohashi, S. Yoshimoto, Removal of organic substances from water by ozone treatment followed by biological activated carbon, *Water Sci. Technol.* 35 (7) (1997) 171–178.
- [38] J. Tanaka, M. Matsumura, Application of ozone treatment for ammonia removal in spent brine, *Adv. Environ. Res.* 7 (2003) 838–845.
- [39] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation process: a general review, *Appl. Catal. B: Environ.* 47 (2004) 219–256.
- [40] J. Rivera-Utrilla, M. Sánchez-Polo, M.A. Mondaca, C.A. Zaror, Effect of ozone and ozone-activated carbon treatments on the genotoxic activity of naphthalenesulfonic acids, *J. Chem. Technol. Biotechnol.* 77 (2002) 883–890.
- [41] F.J. Rivas, F. Beltrán, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachate: sequential coagulation—flocculation + chemical oxidation process, *J. Hazard. Mater. B* 116 (2004) 95–102.
- [42] U. Jans, J. Hoigné, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals, *Ozone: Sci. Eng.* 20 (1) (1998) 67–87.
- [43] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of 1,3,6-naphthalenetrisulphonic acid catalyzed by activated carbon in aqueous phase, *Appl. Catal. B: Environ.* 39 (2002) 319–329.
- [44] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, *Appl. Catal. B: Environ.* 46 (2003) 639–669.
- [45] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of naphthalenesulphonic acid in aqueous phase in the presence of activated carbon in aqueous phase, *Langmuir* 20 (2004) 9217–9222.
- [46] F. Wang, D.W. Smith, M.G. El-Din, Application of advanced oxidation methods for landfill leachate treatment—a review, *J. Environ. Eng. Sci.* 2 (6) (2003) 413–427.
- [47] J. Staehelin, R.E. Buhler, J. Hoigné, Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO₂ as chain intermediates, *J. Phys. Chem.* 88 (24) (1984) 5999–6004.
- [48] B. Legube, N.K.V. Leitner, Catalytic ozonation: a promising advanced oxidation technology for water treatment, *Catal. Today* 53 (1999) 61–72.
- [49] F.J. Beltran, B. Acedo, F.J. Rivas, O. Gimeno, Pyruvic acid removal from water by the simultaneous action of ozone and activated carbon, *Ozone: Sci. Eng.* 27 (2005) 159–169.
- [50] J. Ma, M.H. Sui, Z.L. Chen, L.N. Wang, Degradation of refractory organic pollutants by catalytic ozonation-activated carbon and Mn-loaded activated carbon as catalysts, *Ozone: Sci. Eng.* 26 (2004) 3–10.
- [51] C. Gottschalk, J.A. Libra, A. Saupe, Ozonation of Water and Wastewater: A Practical Guide to Understanding Ozone and its Application, Wiley-VCH, London, 2000.
- [52] J. Rivera-Utrilla, M. Sánchez-Polo, Degradation and removal of naphthalene-sulphonic acids by means of adsorption and ozonation catalyzed by activated carbon in water, *Water Resour. Res.* 39 (9) (2003) 1232–1245.
- [53] J. Rivera-Utrilla, M. Sánchez-Polo, Effect of the ozone-carbon reaction on the catalytic activity of activated carbon during the degrada-

- tion of 1,3,6-naphthalenetri-sulphonicacid with ozone, *Carbon* 41 (2003) 303–307.
- [54] U. Gunten, Ozonation of drinking water. Part I. Oxidation kinetics and product formation, *Water Res.* 37 (2003) 1443–1467.
- [55] T.A. Kurniawan, G.Y.S. Chan, Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate, *Chem. Eng. J.* (2006).
- [56] J.P. Chen, X.Y. Wang, Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns, *Sep. Purif. Technol.* 19 (2000) 157–167.
- [57] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, *Chemosphere* 54 (7) (2004) 951–967.
- [58] N.Q. Zhao, N. Wei, J.J. Li, Z.J. Qiao, J. Cui, F. He, Surface properties of chemically modified activated carbons for adsorption rate of Cr(VI), *Chem. Eng. J.* 155 (2005) 133–138.
- [59] T.A. Kurniawan, A Research Study on Cr(VI) Removal from Electroplating Wastewater Using Chemically Modified Low-cost Adsorbents and Commercial Activated Carbon, Master Thesis, Sirindhorn International Institute of Technology (SIIT), Thammasat University, Pathumthani, 2002.
- [60] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Removal of refractory contaminants from stabilized landfill leachate using ozone-oxidized granular activated carbon (GAC), in: *Proceedings of the Fifth International Symposium on Wastewater Reclamation and Reuse for Sustainability*, Jeju, Korea, 8–11 November, 2005.
- [61] B. Calli, B. Mertoglu, B. Inanc, Landfill leachate management in Istanbul: applications and alternatives, *Chemosphere* 59 (2005) 819–829.
- [62] A. Chianese, R. Ranauro, N. Verdone, Treatment of landfill leachate by reverse osmosis, *Water Res.* 33 (1999) 647–652.
- [63] T.A. Peters, Purification of landfill leachate with reverse osmosis and nanofiltration, *Desalination* 119 (1998) 289–293.
- [64] M.F. Wang, M.G. El-Din, D.W. Smith, Oxidation of aged raw landfill leachate with O₃ only and O₃/H₂O₂: treatment efficiency and molecular size distribution analysis, *Ozone: Sci. Eng.* 26 (2004) 287–298.
- [65] J.M. Jans, A. Schroeff, A. Jaap, Combination of UASB pre-treatment and reverse osmosis, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), *Landfilling of Waste Leachate*, Elsevier, Amsterdam, 1992, pp. 313–321.
- [66] G. Baumgarten, C.F. Seyfried, Experiences and new developments in biological pre-treatment and physical post-treatment of landfill leachate, *Water Sci. Technol.* 34 (1996) 445–453.
- [67] L.D. Palma, P. Ferrantelli, C. Merli, E. Petrucci, Treatment of industrial landfill leachate by means of evaporation and reverse osmosis, *Waste Manage.* 22 (2002) 951–955.
- [68] R. Rautenbach, R. Mellis, Wastewater treatment by a combination of bioreactor and nano-filtration, *Desalination* 95 (1994) 171–188.
- [69] M. Pirbazari, V. Ravindran, B.N. Badriyha, S.H. Kim, Hybrid membrane filtration process for leachate treatment, *Water Res.* 30 (1996) 2691–2706.
- [70] S.H. Gau, F.S. Chang, Improved Fenton method to remove recalcitrant organics in landfill leachate, *Water Sci. Technol.* 43 (1996) 315–322.
- [71] B. Weber, F. Holz, Combination of activated sludge pre-treatment and reverse osmosis, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), *Landfilling of Waste Leachate*, Elsevier, Amsterdam, 1992, pp. 323–332.
- [72] S.M. Hurd, Low Pressure Reverse Osmosis Membrane for Treatment of Landfill Leachate, Master Thesis, The University of Carleton, Ottawa, 1999.
- [73] K.P. Tsagarakis, D.D. Mara, A.N. Angelakis, Application of cost criteria for selection of municipal wastewater treatment systems, *Water Air Soil Pollut.* 142 (2003) 187–210.
- [74] M. Altinbaş, C. Yangin, I. Ozturk, Struvite precipitation from anaerobically treated municipal and landfill wastewaters, *Water Sci. Technol.* 46 (2002) 271–278.
- [75] T.A. Peters, Past and future of membrane filtration for the purification of landfill leachate, in: *Proceedings of the Seventh International Landfill Symposium*, Sardinia, Italy, 1999, pp. 335–344.
- [76] K. Haarstad, T. Mæhlum, Important aspects of long-term production and treatment of municipal solid waste leachate, *Waste Manage. Res.* 17 (1999) 470–477.
- [77] J. Ketter, R. Steegmans, C. Maurer, Optimization and cost reduction in biological-chemical oxidative landfill treatment, in: *Proceedings of the Fifth International Landfill Symposium*, Sardinia, Italy, 1995, pp. 559–566.
- [78] A. Guaiumi, R. Loschi, Leachate treatment through a combined process of evaporation and thermal oxidation, in: *Proceedings of the Fifth International Landfill Symposium*, Sardinia, Italy, 1995, pp. 575–581.
- [79] M. Ettala, E. Rossi, Leachate treatment with a new evaporation technology, in: *Proceedings of the Fifth International Symposium*, Sardinia, Italia, 1995, pp. 583–590.
- [80] R.H. Kadlec, Constructed wetlands for treating landfill leachate, in: G. Mulamootil, E.A. McBean, F. Rovers (Eds.), *Constructed Wetlands for the Treatment of Landfill Leachate*, Lewis Publishers, Florida, 1999, pp. 17–30.
- [81] A. El-Gendi, Leachate Treatment using Natural Systems, PhD Thesis, The University of Windsor, Ontario, 2003.