

# Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems

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## Abstract

In the search for an efficient and economical method to treat a leachate generated from a controlled municipal solid waste landfill site (Jebel Chakir) in the region of greater Tunis in Tunisia, ozone alone and ozone combined with hydrogen peroxide were studied. The leachate was characterised by high COD, low biodegradability and intense dark colour. A purpose-built reactor, to avoid foaming, was used for the study. It was found that ozone efficacy was almost doubled when combined with hydrogen peroxide at 2 g/L but higher H<sub>2</sub>O<sub>2</sub> concentrations gave lower performances. Enhancement in the leachate biodegradability from about 0.1 to about 0.7 was achieved by the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Insignificant changes in pH that may be due to buffering effect of bicarbonate was found. A small decrease in sulphate concentrations were also observed. In contrast, chloride concentration declined at the beginning of the experiment then increased to reach its initial value. Estimates of the operating costs were made for comparison purposes and it was found that the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system at 2 g/L H<sub>2</sub>O<sub>2</sub> gave the lowest cost of about 3.1 TND (~2.3 USD)/kg COD removed.

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## 1. Introduction

The disposal of solid wastes in landfills is the most common practice in developed and developing countries. When water infiltrates through the solid waste, it dissolves and transports a variety of organic and inorganic pollutants, which may leach out if the moisture content of the solid waste is larger than its field capacity (i.e. the upper limit of the solid material ability to absorb water). The quantity of these leachates is small as compared to other wastewaters, but their contents are extremely hazardous [1–3]. These leachates may migrate from the refuse and contaminate surface and ground waters, which may affect human health and the aquatic environment. Treatment of these leachates in classical wastewater treatment plants is rarely practiced due to the nature and high levels of pollutants present in them (i.e. high COD, low biodegradability, heavy metals, pathogens, etc.). Dedicated treatment facilities are therefore required before the

leachate being discharged to the environment or to the sewer system. Depending on the leachate characteristics, operating and capital costs, and regulations, various site-specific treatment techniques can be used to treat these hazardous wastewaters (e.g. coagulation/flocculation, biological, oxidation, AOPs, membrane, leachate recirculation through the landfill, grassland spray irrigation, constructed wetlands, etc.) [4].

Ozonation processes are attractive means for the treatment of landfill leachates due to the high oxidative power that ozone possesses [5–7]. Ozone is particularly effective in the removal of colour and water disinfection [8,9]. Ozone processes can be made more effective for example at high pH (O<sub>3</sub>/OH<sup>-</sup>) and by the addition of hydrogen peroxide (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>). These systems favour the production of hydroxyl radicals (•OH), which are highly reactive species. OH<sup>-</sup> and H<sub>2</sub>O<sub>2</sub> initiate a series of radical reactions that enhance ozone decomposition to yield •OH [10–12]. In the system O<sub>3</sub>/OH<sup>-</sup>, the hydroxide ion reacts with ozone to yield superoxide anion radicals (O<sub>2</sub>•<sup>-</sup>), which in their turn are involved in a series of reactions that yield •OH. Overall 1.5 mol of O<sub>3</sub> yields 1 mol of •OH. In the system O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, when H<sub>2</sub>O<sub>2</sub> is dissolved in water, it partially dissociates into

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### Nomenclature

BOD <sub>5</sub>	5-day biological oxygen demand (mg/L)
C <sub>AG</sub>	off-gas ozone concentration (g/m <sup>3</sup> )
C <sub>AG0</sub>	input ozone concentration (g/m <sup>3</sup> )
CN	colour number (cm <sup>-1</sup> )
COD	chemical oxygen demand (mg/L)
COD <sub>0</sub>	initial COD (mg/L)
NTP	normal temperature and pressure
OC	ozone consumption (kg O <sub>3</sub> /kg ΔCOD)
Q <sub>G</sub>	gas flow rate (mL/min)
SAC	spectral absorption coefficient
t	time (min)
V	reactor volume (mL)

hydroperoxide ion (HO<sub>2</sub><sup>-</sup>, the conjugate base of hydrogen peroxide), which reacts rapidly with ozone to initiate a radical chain mechanism that leads to hydroxyl radicals [13,14]. Overall 1 mol of O<sub>3</sub> yields 1 mol of •OH. Hydroxyl radicals are very reactive, non-selective oxidants, and are the most important species in an advanced oxidation process. Thus ozone-based advanced oxidation processes are attractive processes to oxidise the complex leachate mixtures. It is expected that such processes would oxidise the large refractory organic molecules (up to 10<sup>4</sup> g/mol), found in leachates, to smaller more biodegradable molecules that can be removed in a subsequent biological system. For example in Germany systems such as Bio-O<sub>3</sub>-Bio have been used for the treatment of leachates [8]. However, the presence of certain compounds in the leachate, mainly carbonates and to a lesser extent chlorides and sulphates, may inhibit hydroxyl radical oxidation power. Investigation of this inhibitory effect should be taken into consideration when considering advanced oxidation processes for leachate treatment.

In Tunisia, solid waste quantities are increasing due to demographic and rapid urban growth that the country is experiencing. A national programme for managing solid wastes (PRONAGDES) was launched in 1993 and one of the targets of the programme was to build controlled sanitary landfills and to cleanup existing open landfills. Jebel Chakir site was one of the resulted controlled sites and is the largest landfill site in Tunisia used mainly for disposal of domestic solid wastes. Leachates generated by this site are stocked in collecting basins without treatment. These stocked leachates constitute a real threat to the surrounding areas of fauna and flora. Stringent regulations would not allow direct discharge of the leachates neither into a water body nor into the sewer system. Therefore, new treatment processes are needed in order to ensure compliance and safe discharge.

As a result this research was carried out in order to investigate the treatment of Jebel Chakir landfill leachate using ozone-based processes (i.e. O<sub>3</sub> alone and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>). The work was carried out in a laboratory semi-continuous gas/liquid reactor. Lump parameters including colour, COD and BOD<sub>5</sub> were employed to characterise the overall performance of the oxidation systems studied.

## 2. Materials and methods

### 2.1. Jebel Chakir landfill site

Jebel Chakir landfill site is situated at about 10 km southwest Tunis—capital of Tunisia. It is the largest and first controlled landfill site in the country in operation since 1999 serving the Greater Tunis area. It occupies 47 ha over a reserve total area of 126 ha. It receives 2000 tonnes/day of mainly domestic solid wastes of which 68% are organic materials [15,16]. The precipitation in the region is variable throughout the year and has an average value of about 460 mm/year. The site generates around 270 m<sup>3</sup>/day of liquid leachate piped to and stocked in eight collecting basins of total capacity 130,000 m<sup>3</sup>.

### 2.2. Experimental set-up

Leachate samples were collected from a storage basin (over 6 years old) on a winter day ( $T=17\text{ }^{\circ}\text{C}$ ) in drums and transported to the laboratory, which is situated at about 1 hour drive from the site. A 20 L quantity of the leachate was refrigerated immediately and used in this study. The leachate used in this study is classified as of intermediate age tending to stabilisation. A schematic of the experimental set-up is shown in Fig. 1. The system consisted of a 150 mL glass reactor fed with ozone in oxygen through a glass sinter gas diffuser. A magnetic stirrer was used to ensure well mixing in the reactor. Ozone was produced using a BMT 803 generator (BMT Messtechnik, Germany) fed by dry pure oxygen. Gas ozone concentration (in g/m<sup>3</sup> NTP) was measured by an ultraviolet gas ozone analyser (BMT 963). A soap bubble digital calibrated flow meter (Shimadzu DFM-140) was used to measure the gas flow rate in mL/min. As was expected, foaming problem did occur once the gas passed through the leachate that may due to the presence of surfactants. This has led to modify the system and introduce a foam destructor followed by a gas/liquid separator. This system proved to

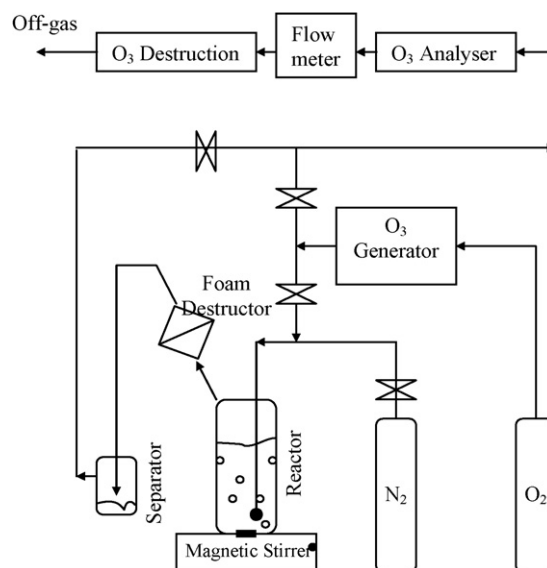


Fig. 1. Experimental set-up.

work well and a total loss in liquid of less than 5 mL (~3%) was never exceeded over a 60 min experiment. A nitrogen supply was fitted to the system to purge any residual ozone left in solution at the end of an experiment. By measuring  $N_2$  flow rate and gas  $O_3$  concentration, the dissolved ozone concentration could be determined. Ozone in the off-gas was converted to oxygen using an alumina catalyst followed by a KI solution and the whole experimental system was placed under fume cupboard. Due to analysis requirement and the small volume of reactor, samples were not withdrawn during an experiment but instead the whole volume was used at the end of an experiment scheduled for a given time. The gas flow rate was  $200 \text{ mL/min} \pm 10\%$  and the input ozone concentration was about  $80 \text{ g/m}^3 \text{ NTP} \pm 0.5\%$ . All experiments were conducted at room temperature of  $20 \pm 3 \text{ }^\circ\text{C}$ . Hydrogen peroxide was added to the leachate at concentrations up to  $12 \text{ g/L} \pm 2\%$ . The leachate solution has showed buffering behaviour in all experiments, which ensured constant pH at about  $8.7 \pm 0.2$  without the addition of any buffering medium.

### 2.3. Analytical methods

Standard methods were used to characterise the leachate. COD measurements were performed using a Behr COD workstation according to DIN 38409. Relative error for COD measurement was estimated to about 10%.  $BOD_5$  was measured using the respirometric method by measuring oxygen pressure decrease using Oxitop<sup>®</sup> bottles (10% relative error). TOC measurements were performed using Euroglass TOC 1200 instrument according to NF EN 1484 (10% relative error). All metal analyses were performed using an atomic absorption spectrometer Perkin-Elmer Analyst 200. Chloride and sulphate were analysed using an ionic chromatograph (Waters—water column IC), and phosphate was measured according to the vanadomolybdophosphoric acid colorimetric method. A pH meter, Orion 420A, was used for pH measurement. Gas phase ozone concentrations were determined using a BMT 963 ozone analyser (BMT Messtechnik). In order to stop ozone reaction at the end of an experiment, a stream of nitrogen was used to purge any residual ozone. This procedure was also useful to determine dissolved ozone concentration,  $C_{AL}$ , at the end of each experiment by measuring  $N_2$  flow rate and the off-gas ozone concentration,  $C_{AG}$ . The product of  $N_2$  flow rate by the integral of  $C_{AG}$  over

Table 1  
Jebel Chakir leachate characteristics

Parameter	Concentration (mg/L) except pH	Parameter	Concentration (mg/L)
pH	8.7	P	8.79
COD	5230	Cr	2.24
$BOD_5$	500	Cu	0.14
$HCO_3^-$	21750	Zn	0.94
$Cl^-$	4870	Ni	0.53
$SO_4^{2-}$	76	$Ca^{2+}$ and $Mg^{2+}$	2000

time gave the amount of residual ozone in the liquid phase and in the known gas dead-volume; by subtraction,  $C_{AL}$  was calculated.

## 3. Results and discussion

### 3.1. Leachate characteristics

Some of the characteristics of the leachate used in this work are presented in Table 1. It is an alkaline mixture of dark brown colour. It has high COD value but low biodegradability ( $BOD_5/COD \approx 0.1$ ). The COD value is much higher than that of domestic wastewater and it is higher than the Tunisian Standards for discharge in public sewer (NT 106 002: COD = 1000 mg/L and  $BOD_5 = 400 \text{ mg/L}$ ), therefore a discharge into the sewer is not permitted. It is particularly to note the high concentration of bicarbonates and chlorides that may influence the advanced oxidation process through the scavenging effect of hydroxyl radicals. Notwithstanding, the high value for bicarbonates concentration may prevent significant lowering in the alkaline pH following the ozonation process. This may be beneficial since alkaline condition helps with hydroxyl radical production through ozone decomposition by the hydroxide ion  $OH^-$  [13]. The characteristics of the leachate used in this study as presented in Table 1 are comparable to those obtained by [17–23] and are within the range of values presented in [2].

### 3.2. Off-gas ozone concentration

Fig. 2(A) shows the change with time of the off-gas ozone concentration ( $C_{AG}$ ). It shows that all graphs for the different

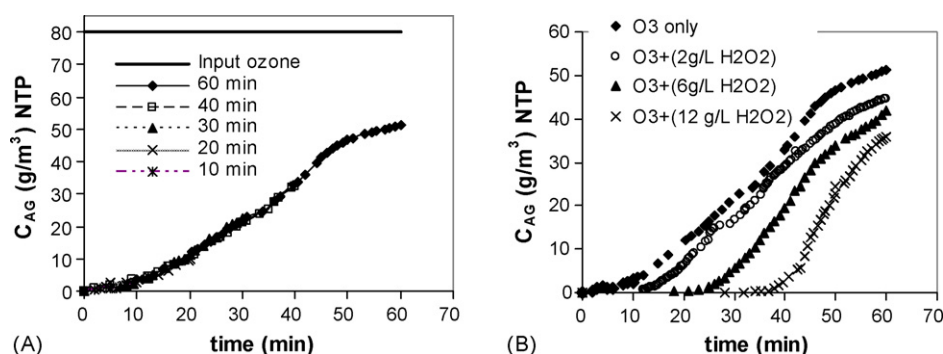


Fig. 2. Evolution of the off-gas ozone concentration as function of treatment time. (A) Reproducibility of results:  $O_3$  alone system. (B) Comparison between  $O_3$  alone and  $O_3/H_2O_2$  systems.

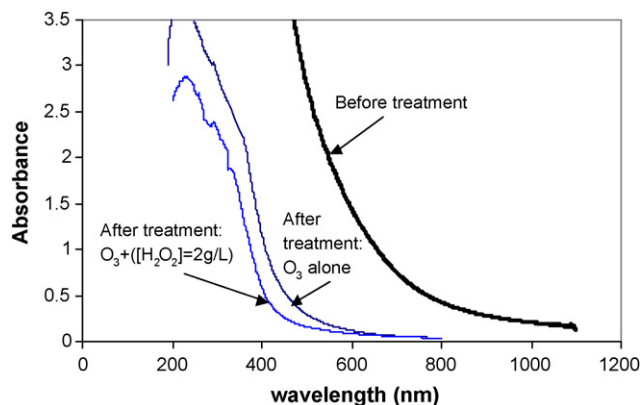


Fig. 3. UV/vis spectra of the leachate before and after treatment with  $O_3$  alone and  $O_3/H_2O_2$ .

experiments overlap, which proves the reproducibility of results and the validity of the experimental procedure. Ozone concentration increases slowly at the outlet of the reactor for the first 10 min in the case of  $O_3$  alone, this behaviour is characteristic of a fast kinetic regime of ozone reactions at the beginning of the experiment [24]. Since the pH of the mixture is alkaline (pH 8.7), the total reaction of ozone may be due to direct reactions of the  $O_3$  molecule with the susceptible elements present in the leachate and may also be due to ozone decomposition that forms high reactive hydroxyl radicals at such a high pH [13]. After this period the increase in  $O_3$  concentration is more or less exponential following a change to an intermediate kinetic regime due to a decrease in pollutant concentration. After approximately 50 min of ozone bubbling,  $C_{AG}$  starts to level off at a value much lower than the input ozone concentration. This is an indication that ozone reactions are still taking place probably with products from the initial reactions. The kinetic regimes discussed earlier were also confirmed by almost nil dissolved ozone concentrations obtained at the end of the short-time experiments. If the experiments were carried out for much longer times than 60 min, it is expected that  $C_{AG}$  would level off at approximately the input ozone concentration value and the dissolved ozone concentration would increase and stabilise at a value close to equilibrium concentration. Similar behaviour was also obtained for  $O_3/H_2O_2$  system Fig. 2(B), but the first period of fast kinetics took longer in this case up to 40 min depending on  $[H_2O_2]$ . Although the off-gas ozone concentration for the  $O_3/H_2O_2$  system remained almost nil for longer times, it does not indicate that pollutant degradation is high as consequence. In reality complex radical reactions contribute to ozone consumption under the conditions of the experiments (high pH and high  $[H_2O_2]$ ), which lead to the formation of  $\bullet OH$  that would increase further ozone destruction, thus inhibit part of the ozone from reacting with the target compounds.

### 3.3. Colour removal

Fig. 3 shows the spectra obtained before treatment and after treatment with ozone alone and ozone combined with hydrogen peroxide at 2 g/L. It is clear from Fig. 3 that absorbance at all wavelengths was reduced following treatment and more reduc-

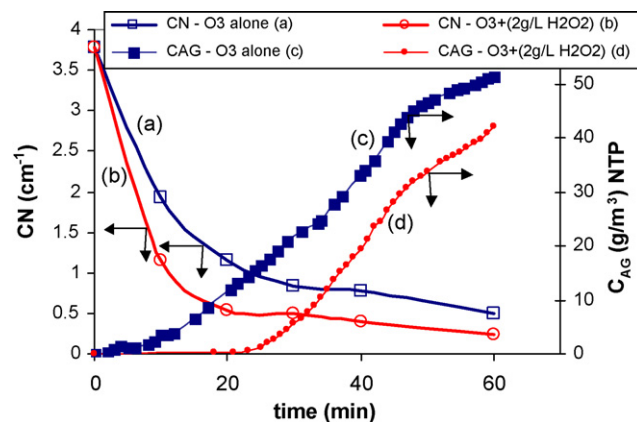


Fig. 4. Evolution of the colour number and the off-gas ozone concentration as function of treatment time.

tion was obtained when  $H_2O_2$  was added. However, when only hydrogen peroxide without ozone was used, only insignificant reduction in colour was observed (this result is not shown in here).

Since the visible region of the leachate spectrum showed no limited absorption maxima (Fig. 3), the colour number CN as defined by Eq. (1) was used to characterise colour [25]. CN relies on the measurement of the spectral absorption coefficient (SAC) in the visible range at wavelengths of 436, 525 and 620 nm. SAC is determined by the absorption value (Abs) in a cell of thickness  $x$  using Eq. (2):

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

$$SAC_i = \frac{Abs_i}{x} \quad (2)$$

The variations of the colour number, CN, with time for  $O_3$  alone and  $O_3/H_2O_2$  treatments are shown in Fig. 4(a) and (b), respectively. The curves (a) and (b) present two kinetic periods each. The first period, (from time zero up to about 12 min), is marked by a rapid decrease in CN values, thus fast kinetics followed by a second period marked by slow changes in CN values, almost a plateau is reached, which corresponds to slow discolouration rates. This change in discolouration kinetics from fast to slow is probably due to changes in ozone reaction mechanisms following changes in the nature of compounds with which ozone reacted (i.e. oxidation by-products). For example the ozonation of aromatic compounds leads for instance to phenols, quinones, aromatic acids and then further oxidation leads to aliphatic acids and aldehydes. Ozone reacts very rapidly with the initial compounds but eventually slowly with the acids and the aldehydes [26–28].

When ozone alone was used, the change from fast to slow kinetics in colour removal occurred almost simultaneously with the change in trend of the off-gas ozone concentration (Fig. 4(c)). In contrast, a change in the trend of the off-gas ozone concentration occurred later (about 22 min) than the change in colour removal kinetics when hydrogen peroxide was added (Fig. 4(d)). This delay supports the hypothesis of the contribution of hydrogen peroxide and the colourless by-products in ozone



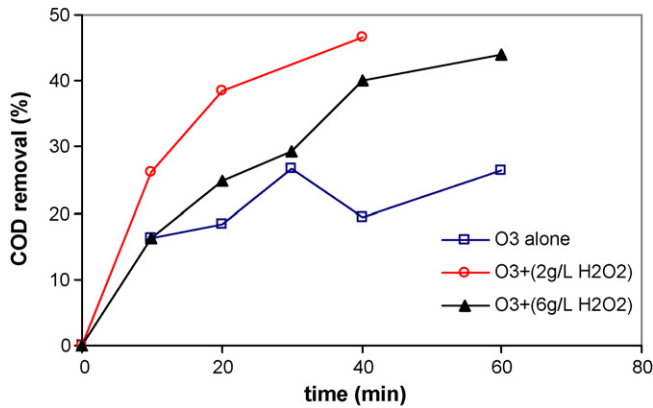


Fig. 5. Influence of initial hydrogen peroxide concentration on COD removal.

consumption; an effect that was not represented by a change in CN.

Looking at the effect of hydrogen peroxide, Fig. 4(a) and (b) shows that H<sub>2</sub>O<sub>2</sub> increased the discolouration rate by almost 50% as compared to ozone alone due to higher hydroxyl radical production in the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Furthermore, the final colour removal was higher for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system (94%) as compared to O<sub>3</sub> alone system (87%). Ozone performance in colour removal is observed in several works; for example Silva et al. [3] obtained 87% reduction in colour following the ozonation of a leachate at an ozone dose of 3 g/L and Ho et al. [29] reported rapid removal of leachate's colour without significant effect on pH changes. Our results for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system were obtained when the initial hydrogen peroxide concentration was 2 g/L, but an increase in the initial [H<sub>2</sub>O<sub>2</sub>] up to 12 g/L decreased the kinetics to values similar to those obtained for ozone alone system (for figure clarity, this result is not shown here). This result was not a surprise but confirmed the concept of a critical hydrogen peroxide concentration above which oxidation rates were reduced as observed in other works [30,31]. In our work, it was found that 2 g/L of hydrogen peroxide is the critical concentration as it will be confirmed in the following paragraphs.

#### 3.4. Effect on chemical oxygen demand and biodegradability

Results for the effect of O<sub>3</sub> alone and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> systems on COD and biodegradability are presented in Figs. 5 and 6. Biodegradability is defined as the ratio of BOD<sub>5</sub> to COD. Fig. 5 shows that ozone alone system ensured COD removal of about 27% after 1 h and the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system has increased COD removal up to 48%. Wang et al. [32] obtained an improvement in COD reduction from 37% for ozone alone to 47% when hydrogen peroxide was added with the ozone system at ozone consumptions (about 6.5 g O<sub>3</sub>/g COD removed) higher than those employed in this work. Wable et al. [33] showed that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> was effective to remove 95% of COD at an ozone dosage of 7 g O<sub>3</sub>/L and a mass ratio of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> = 0.4 g/g. Other ozone-based AOPs have also shown improved COD reductions when used to treat leachates. For example heterogeneous cat-

alytic ozonation (HCO) was successful to reduce COD by 89% at an ozone consumption of 1.5 g O<sub>3</sub>/g COD [34] and by 75% at an ozone consumption of 1.7 g O<sub>3</sub>/g COD removed [35]. In a previous work that employed HCO to treat the leachate used in this study, a decrease in COD by about 45% at an ozone consumption of 1.7 g O<sub>3</sub>/g COD removed was obtained [36]. In addition, Fig. 5 shows that COD removal rate is highest at the beginning of the experiment due to availability of easily oxidisable compounds. Further increase in reaction time led to a slow change in removal rate and a tendency for a level off to a final COD removal value. Concentrations of H<sub>2</sub>O<sub>2</sub> at 2 g/L gave better performance than H<sub>2</sub>O<sub>2</sub> at 6 g/L. This indicates that an increase in hydrogen peroxide level will not always increase COD removal rates. In effect, increasing hydrogen peroxide concentration will change its role from being initiator for the production of hydroxyl radicals to inhibitor of ozone decomposition through free radical reactions. As a consequence, COD removal rate diminishes. Similarly to colour removal, hydrogen peroxide concentration of 2 g/L seems also optimal for COD removal.

Fig. 6 shows that the leachate presented low biodegradability (BOD<sub>5</sub>/COD = 0.1), which was not enhanced when both systems were used except for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system at [H<sub>2</sub>O<sub>2</sub>] = 2 g/L that gave a biodegradability value of 0.7. Several studies have also shown improvement in biodegradability following treatment of leachates with AOPs particularly those based on ozone [5,17,35–37]. Bila et al. [17] used ozone in conjunction with a physicochemical and biological systems and found that ozonation alone was capable to enhance biodegradability from 0.05 to 0.3 at an ozone dose of 3 g/L and reduce COD by about 50%. A Fenton process (Fe<sup>2+</sup> + H<sub>2</sub>O<sub>2</sub> + H<sup>+</sup>) was tested by Lopez et al. [37] to treat a mature leachate. The process enhanced biodegradability from 0.2 to 0.5 and reduced COD by 60%, but this system involved reduction in pH from 8.2 to 3.0 for best operating conditions of the Fenton process followed by increase of the pH to 8.5 for removal of residual ferric ions and to permit a subsequent biological treatment. Our work showed good enhancement of biodegradability by the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system, which is a very important result, indeed a process of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> followed by a biological treatment could be an economical means for the treatment of this leachate. But further studies on biological

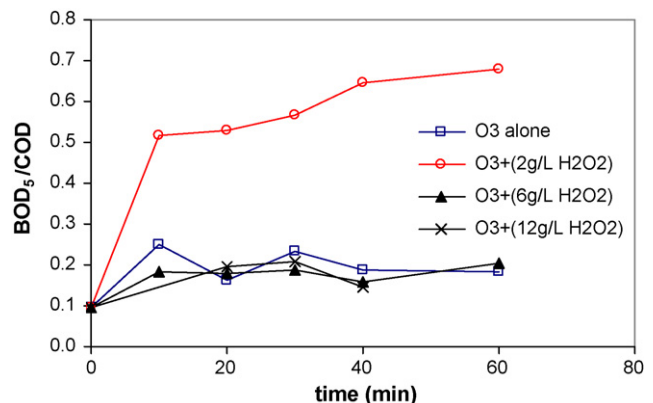


Fig. 6. Influence of initial hydrogen peroxide concentration on biodegradability.

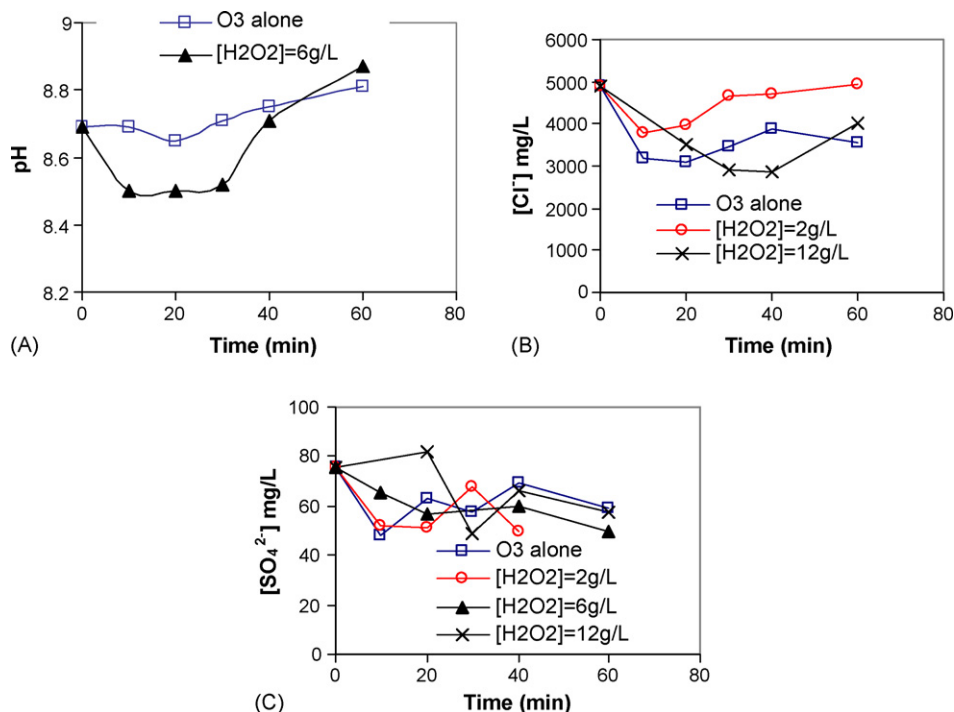


Fig. 7. Evolution of pH (A), chlorides (B), and sulphates (C) as function of treatment time.

treatment in conjunction with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment are required to ascertain this statement. Here again as being expected, the scavenging effect of hydrogen peroxide presented a barrier for treatment improvement. It is therefore always inevitable to search for an optimal hydrogen peroxide concentration above which a decline or no effect of H<sub>2</sub>O<sub>2</sub> on treatment would be observed [30,31]. Hydrogen peroxide concentration of 2 g/L remained optimal for the three parameters studied so far (i.e. colour and COD removals, and biodegradability enhancement).

### 3.5. Effect on pH, chlorides and sulphates

Evolution of pH, and chloride and sulphate ions is shown in Fig. 7(A)–(C). It was found that the pH presented only a slight change of less than 0.4 pH units in all experiments and remained constant at about 8.7 on average. Though, it was expected that ozonation would decrease the pH to acidic values due to the formation of carboxylic acids [38–41]. pH lowering was not observed in this work because it may be due to the buffering effect that would impart bicarbonates (Table 1). Bicarbonates buffer the pH by reacting with any acids added to the system following oxidation of the organic matter. They may result from certain construction and demolition wastes, which can always end up in the landfill, and from the decomposition of organic matter. Initially, lower pH values by about 0.2 pH units were obtained with the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system as compared to O<sub>3</sub> alone Fig. 7(A). This small lowering in pH may be attributed to hydrogen peroxide, which is a weak acid (H<sub>2</sub>O<sub>2</sub> ⇌ HO<sub>2</sub><sup>-</sup> + H<sup>+</sup>, pK<sub>a</sub> = 11.6). Several studies have also shown small changes in pH following ozonation of a leachate [5,29,36].

For chlorides, it was observed that Cl<sup>-</sup> concentration has declined at the beginning of the experiment followed, after about

30 min, by slow increase in concentration towards its initial value (Fig. 7(B)). Chlorides can react with both ozone and hydroxyl radicals, which may explain the decrease in chlorides at the start of the experiment due to high oxidants availability (reactions (I) and (II)) [42]. Following this initial period, chlorides would reappear as shown by reaction (III). It is most probable that reaction (III) would dominate reaction (II) due to availability of molecular ozone and due to its high rate constant as compared to reaction (II):

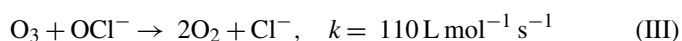
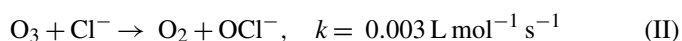
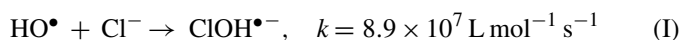
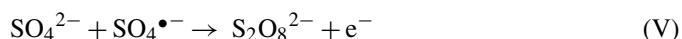


Fig. 7(C) shows an overall decrease in sulphate ions content. It is known that sulphate ions do not react with molecular ozone, but radical reactions are possible as shown by reactions (IV) and (V). Thus the decrease in sulphate concentration could be attributed to these reactions. It is to note here that although sulphate ions contribute to hydroxyl radical consumption, which may reduce the performance of the oxidation process, the formed radical SO<sub>4</sub><sup>•-</sup> may contribute to the overall oxidation process [43]:



### 3.6. Ozone consumption and cost estimate

Ozone consumption, OC, is an important parameter in ozone processes since it can be correlated to the operating costs. It

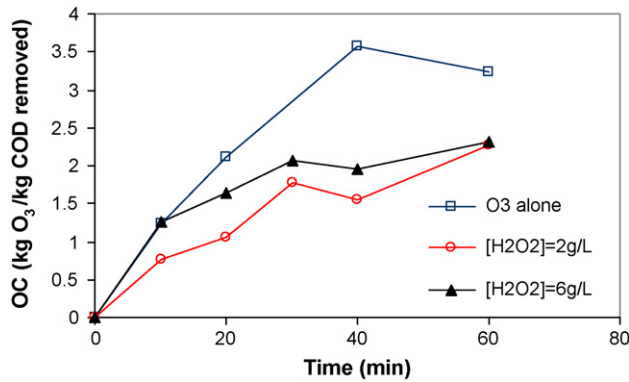


Fig. 8. Evolution of ozone consumption as function of treatment time.

is defined as the amount of ozone consumed for a given mass of COD removed, Eq. (3). It is anticipated to operate at low OC values in order to maximise ozone utilisation and thus reduce costs. The variation of OC with time for both systems is shown in Fig. 8. The ozone alone system presented the highest values for OC and the lowest ones were obtained for the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Table 2 gives OC values for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> at different hydrogen peroxide concentrations after 40 min operational time. Here again a hydrogen peroxide concentration of 2 g/L is optimal for ozone consumption as it shows the lowest OC value of 1.5 kg O<sub>3</sub>/kg COD removed. The literature cited ozone consumption values from less than 1 kg O<sub>3</sub>/kg COD [29] up to 16 kg O<sub>3</sub>/kg COD [32] and typical values are between 2 and 3 for ozone alone systems [23]. The variations in ozone consumption shown in literature are due mainly to the wide variations of the characteristics of the leachates studied (e.g. leachate age, pH, organic composition, •OH scavengers, etc.). Typically for intermediate COD removal (about 50%), when ozone-based AOPs are used, ozone consumption values are about 1.5 kg O<sub>3</sub>/kg COD [34–36], but they increase up to 3.5 kg O<sub>3</sub>/kg COD when the target COD removal is high (about 95%) [33].

Operating cost estimates per kg of COD removed were calculated. For the sake of calculation it was assumed that: (i) ozone power consumption was 10 kWh/kg O<sub>3</sub>; (ii) the cost of a power unit was 0.1 TND/kWh (TND, Tunisian Dinar; 1 TND ≈ 0.75 USD); (iii) the cost of hydrogen peroxide at 30% was 0.5 TND/L; (iv) the operating time was 40 min. The calculated cost figures were 4.2, 3.1 and 6.8 TND/kg COD removed for hydrogen peroxide concentrations of 0.0, 2.0 and 6.0 g/L, respectively. These values show that the lowest cost was 3.1 TND (~2.3 USD)/kg COD removed obtained for the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system at 2 g/L H<sub>2</sub>O<sub>2</sub>. Schulte et al. [11] have also showed that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system was the least expensive process

Table 2  
Ozone consumption after 40 min

	[H <sub>2</sub> O <sub>2</sub> ] (g/L)		
	0	2	6
COD removal (%)	19.3	46.6	40.1
OC (kg O <sub>3</sub> /kg COD)	3.6	1.5	1.9

to treat hazardous wastes. Although it is difficult to obtain reliable cost figures in the literature, results obtained in this work are comparable to (1.34 Euro (~1.5 USD)/kg COD) presented in [44] but are about three times lower than (~7.5 USD/kg COD) presented in [11]. It is to note that these cost figures should be treated with caution as accurate cost estimate is difficult to make since costs may change daily following for example fluctuations in energy prices. The figures presented here are for comparison purposes only.

$$OC = \frac{Q_G \int_0^t (C_{AG0}/C_{AG}) dt}{V (COD_0 - COD)} \quad (3)$$

where  $Q_G$  is the gas flow rate,  $V$  the reactor volume,  $C_{AG}$  the off-gas ozone concentration,  $C_{AG0}$  the input ozone concentration,  $t$  the time and  $COD_0$  and  $COD$  is the initial and final COD.

#### 4. Conclusions

This work has shown the performances of O<sub>3</sub> alone and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>-based advanced oxidation systems to treat the intermediary Jebel Chakir site landfill leachate. The leachate is characterised by high COD values up to 5230 mg/L, very low biodegradability (BOD<sub>5</sub>/COD = 0.1) and an intense dark colour. The study showed that ozone combined with hydrogen peroxide is an efficient method to treat this leachate. The main conclusions and suggestions for future studies are:

- COD reductions of up to 48%, biodegradability of 0.7 and colour removal of 94% were achieved after treatment with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system.
- Hydrogen peroxide proved to enhance the treatment process when combined with ozone as compared to ozone alone or hydrogen peroxide alone.
- An optimal hydrogen peroxide concentration of 2 g/L was a limiting concentration above which a decline in removal rates and biodegradability and an increase in operating costs were observed. This shows that it is important to investigate the effect of hydrogen peroxide concentration on the treatment efficiency in order to determine H<sub>2</sub>O<sub>2</sub> optimal concentration.
- Both molecular ozone and hydroxyl radicals were responsible for oxidation reactions.
- Measurement of ozone concentration in the off-gas revealed that fast kinetic regime at the beginning of the experiment followed by a change to intermediate kinetics governed the oxidation process.
- The leachate has shown small changes in pH that may due to buffering effect of bicarbonates.
- A decrease in chlorides at the beginning of the experiment followed by re-establishment of its initial concentration was observed.
- A clear decrease in sulphates was observed that may due to hydroxyl radical reactions.
- For comparison purposes only, estimates of operating costs were calculated. It was found that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> at 2 g/L gave the lowest cost (3.1 TND (~2.3 USD)/kg COD removed).

- For future work, it is anticipated to study the biological treatment of the leachate following its treatment with  $O_3/H_2O_2$ .

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