Decomposition of toxic pollutants in landfill leachate by ozone after coagulation treatment

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Abstract

This study deals with evaluation of organic matter from Mexico City waste sanitary landfill leachate of Bordo Poniente (including domestic and industrial) by ozonation after a coagulation treatment with $Fe_2(SO_4)_3$ (2.5 g/L at pH 4–5). The content of humic substances after the coagulation treatment decreases up to 70%. Then leachate obtained from a solid with initial COD = 1511 mg/L and the pH 8.5 was treated by ozone. The aqueous samples by a UV–vis and HPLC technique were analyzed. The partial identification of the initial composition of the organic matter as well as of intermediates and final products was carried out after the extraction of the initial and ozonated leachate with benzene, chloroform:methanol (2:1) and hexane. Then the extracts with a gas chromatograph with mass detector and FID were analyzed. In the HPLC results we identify malonic and oxalic acids. The initial concentrations of these acids were 19 mg/L and 214 mg/L, respectively. The oxalic acid is formatted and accumulated in ozonation. The obtained results show that the color disappears (visually) at 100% during 5 min of ozonation. The organic substances, extracted with chloroform–methanol, may be destructed during 15 min of ozonation; the organic matter, extracted with benzene, destructs completely by ozone during 5 min, and the organic compounds extracted with hexane have a low ozonation rate. The toxic compounds presented in leachate decompose completely during 15 min of ozonation. The ozonation rate constants for each group of organics (as observed constants) were calculated applying simplified mathematical model and the recurrent least square method using the program MATLAB 6.5.
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1. Introduction

Economic considerations continue to maintain landfills as the most attractive option for municipal solid waste disposal. Alternative methods to landfilling (incineration and composting) are actually considered as volume reduction process, since they produce waste fractions (ashes and slag) which ultimately must be landfilled [1–3]. Despite the evolution of landfill technology, from open uncontrolled dumps to highly engineered facilities designed to eliminate or minimize the potential adverse impact of the waste on the surrounding environment, the generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfills. Leachate is formed when the refuse moisture content exceeds its field capacity, which is defined as the maximum moisture that can be retained in a porous medium without downward percolation [4].

There are many factors related to the quality and quantity of the water formed at landfills: seasonal weather variations, landfilling technique, phase sequencing, piling and compaction method, etc. Organic and inorganic contaminants of landfill leachates are released from waste due to successive biological, chemical and physical processes [5–7]. Also, refuse and composition, pretreatment, biological stage, age and structure of the landfill has an influence to the amount and composition of leachates at a landfill site [8–10]. According to numerous authors, three types of leachates can be classified by landfill age: young, intermediate and stabilized (Table 1). In general, young leachate is highly contaminated with organic compounds, ammonia, halogenated hydrocarbons and heavy metals. The humic substances (HS) constitute an important group of leachate organic matter [9,11,12]. Nevertheless, the principal components of organic compounds in landfill leachates do not vary

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Table 1
Leachate classification [5,10,42]

Leachate type	Young	Intermediate	Stabilized
Landfill age (years)	<5	5–10	>10
pH	<6.5	6.5–7.5	>7.5
COD (mg/L)	>20,000	3000–5000	<5000
BOD$_5$/COD	>0.3	0.1–0.3	<0.1
Organic matter VFA (%TOC)	70–90	20–30	5
HMW (%TOC)	–	–	>60
Kjeldhal nitrogen (mg/L)	100–2000	–	–
Metals (g/L)	2	<2	<2

VFA: volatile fatty acids; HMW: high molecular weight humic and fulvic-like material.

significantly: only the composition of organics can be varied dependently on the landfill age (Table 2) [8,9,13–17]. In addition, with increasing landfill age, the produced leachates are characterized by the presence of substantial quantities of recalcitrant, difficult-to-treat, "hard" COD (the chemical oxygen demands) compounds. The degradation of organic matter, using various treatments as electrochemical oxidation [18], by coagulation–flocculation [5,19–21], chemical precipitation and activated carbon adsorption [22], membranes [23,24], combination of coagulation, flocculation and chemical oxidation [25], advanced oxidation [26], ozonation [27–29], combination of ozonation, Fenton, biodegradation and adsorption onto activated carbon [30] by wet air oxidation at high temperature [31], by electro-Fenton method [32] will obligatorily depend on the chemical make-up of the present organics, and the ambient conditions, which can significantly modify this chemical make-up [11,14]. The great variety of leachate constituents prevents evaluation of the fate and the role played by each component in the environment impact.

Ozone has been suggested as an alternative for the treatment of landfill leachates [33]. It may be used in the beginning (pre-ozonation), in intermediate phase and at the end of the treatment process [34]. In pre-ozonation, the main objective is the decomposition of large organic molecules [35] in order to increase the effectiveness of the following treatment steps such as biodegradation or adsorption in activated carbon [36]. Ozone also is preferable for coagulation [37], for the removal of color, odors and the chemical oxygen demands of leachates, where it avoids

the production of associated sludge's. In the previous research it has been found that ozone is most effective in leachates, which do not contain hard COD using advanced oxidation processes (AOP's) [38].

Referring to the previous study presented above, which the different treatment methods of landfill leachates were described, the contribution of this study is the remediation of toxic pollutants from Mexico City waste sanitary landfill leachate of Bordo Poniente (including domestic and industrial) by ozonation after the coagulation treatment. The initial and ozonated leachate with benzene, chloroform:methanol (2:1) and hexane were extracted to the partial identification by a gas chromatograph with a FID and a mass detector of the initial, intermediates and final products of ozonation. The aqueous samples were analyzed by a UV–vis spectrophotometer and the HPLC technique. The ozonation rate constants (as the observed constants) for each group of extracted organics were calculated using the simplified mathematical model proposed in previous publications [39–41].

2. Materials and methods

2.1. Description of the site and characterization of the waste material

The leachate treated in this study comes from Mexico City waste sanitary landfill of Bordo Poniente (including domestic and industrial waste). The total area of the site is about 1999 ha. Four controlling wells are situated on three old parts with the arias of 74 ha, 80 ha and 104 ha that are closed and the new waste bank was taken into use in 1996, which receive the solid waste about 7000–8000 t/day. To obtain a representative distribution of the leachates organic matter composition, the sampling site was selected into the treatment plant (a deposal tank) where are received inflows from all sites. So it is possible to ensure that the leachates represent the whole condition of the landfill. The samples (300 L of each) were collected in the summer and in the winter during 2 years (1998 and 1999). In order to avoid the samples variations, they were mixed, stored at 4 °C and kept during all experiments [42]. The initial COD is 4580 mg/L with a pH of 8.6.

The content of heavy metal species in the studied leachate is reported in Table 3 (the result of the present work). It coincides with the preliminary investigation results [16,42].

2.2. Coagulation treatment

The coagulation treatment of the studied leachate was carried out by Fe$_2$(SO$_4$)$_3$ as the coagulant at the optimal conditions

Table 2
Composition of the organic compounds of non-stable leachates (references summary)

Compound	Concentration (mg/L)	% of TOC
Aliphatic carboxylic acids	30,000	>95 (volatile fatty acids)
Aromatic carboxylic acids	1000	–
Methylphenols	100	–
Ethylphenols	50	–
Alkylbenzenes	1.21	–
Aliphatic compounds (hydrocarbons, alcohols and ketone)	300	0.04 (0.7 of alcohols)
Amines	300	0.8
Humic and fulvic acids	100–420	1.3

Table 3
Content of heavy metals in leachate

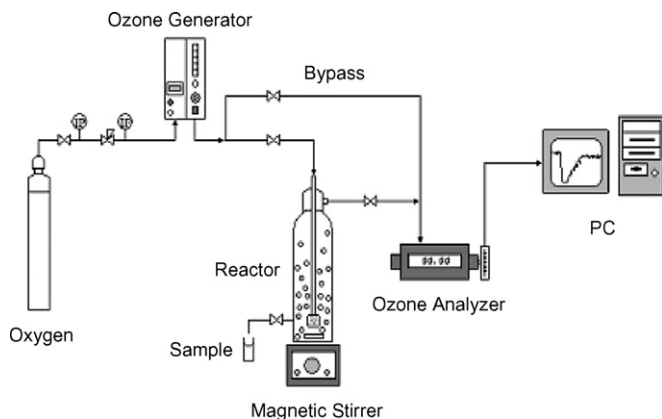| Metal	Concentration (mg/L)
Fe	4.3
Ni	1.2
Cr	0.9
Pb	0.8
Zn	0.5

Fig. 1. Schematic diagram of the ozonation apparatus.

proposed by Monje [42] (at pH 4–7, the coagulant doses was 2400 mg/L, the treatment time was 30 min), which were investigated in detail in Refs. [27,37]. In this study the landfill leachate, obtained from the solid waste after the coagulation treatment with COD 1511 mg/L and pH 8.5 (after the preliminary neutralization), was used in ozonation experiments. In the pretreated leachate after the coagulation treatment the heavy metal species were not found.

2.3. Leachate ozonation

The oxidation of the leachate solution was carried out in a semi batch reactor (500 mL, diameter 5 cm and height 26 cm) using an ozone generator "AZCO" with an ozone concentration of 23 mg/L with the gas flow of 0.5 mL/min. The measurement of ozone in gas phase in the outlet of the reactor was done with an ozone analyzer BMT 930, connected with a PC. The ozone analyzer provides the ozone detection in the gas phase for the ozone monitoring to measure the ozonation degree as well as the ozone consuming and the ozone decomposition. The reactor has a by-pass gas flow. This special reactor construction allows controlling the gas flow into or out of the reactor using the same ozone analyzer. The schematic diagram of the ozonation is shown in Fig. 1.

2.4. Analytical methods

The partial identification of the initial organics composition of leachate, also intermediates and final products of ozonation was carried out by the extraction of the initial and ozonated leachate with benzene, chloroform–methanol (2:1) and hexane for the organics separation based on their chemical structure in three conditional groups: aromatic, polar and aliphatic compounds as it was proposed by Ref. [9]. The samples in the extraction were concentrated with the ratio 100:1. These extracts were analyzed with a gas chromatograph with a mass detector (GC/MS) and FID. The chromatographic analysis conditions with a FID were done using the chromatograph Varian CP 3380 with capillary column Quadrex 007 (methyl 50%–phenyl silicon) 250 mm × 0.25 mm, the sample volume 1 μL, with the temperature programming up 30 °C

to 200 °C during 2 min with 6 °C/min, and at 200 °C during 8 min; with gas flow (nitrogen) 1.4 mL/min; T_{det} 250 °C and T_{inj} 220 °C [8,9,17]. The chromatographic analysis conditions with a mass detector were done using the chromatograph AutoSystem XL, Turbo Mass, Perkin-Elmer with capillary column SPB-225 (30 m × 0.25 mm), the sample volume 1 μL, under the temperature programming from 30 °C up to 220 °C during 5 min with 6 °C/min, and at 220 °C during 8 min; with gas flow (nitrogen) 1.4 mL/min; T_{det} 250 °C and T_{inj} 220 °C.

The aqueous samples were analyzed too by UV–vis spectrophotometer and HPLC technique. The HPLC analysis were done using a liquid chromatograph Perkin-Elmer with UV/vis detector, Series 200, with a mobile phase of water:acetonitrile–phosphoric acid mixture (89.9:10:0.1) with a flow rate of 0.8 mL/min in a Spheri-5 ODS, Silica 5μ, 250 mm × 4.6 mm column. The identification of sub-products at the final reaction was realized comparing the retention time of the UV spectrums of patterns at 210 nm.

The summary information of the organic pollutants decomposition dynamics in water at absorbency from 190 nm to 485 nm was obtained using the spectrophotometer (Perkin-Elmer Lambda 2B). Fig. 2 presents the UV–vis spectrum variation of the original landfill leachate and residual water of leachate during ozonation at pH 8.5. The corresponding characteristic absorbency is at $\lambda = 254$–280 nm [35].

To identify heavy metals in pre-treated samples of leachate the atomic absorption spectrophotometry technique (AA) (Perkin-Elmer), using the standard solutions of Fe, Ni, Cr, Pb and Zn with the concentrations 0.1 ppm, 0.5 ppm, 1.0 ppm and 1.5 ppm, was used. The heavy metal concentrations were measured according to standard methods (APHA, AWWA and WPCF) [43].
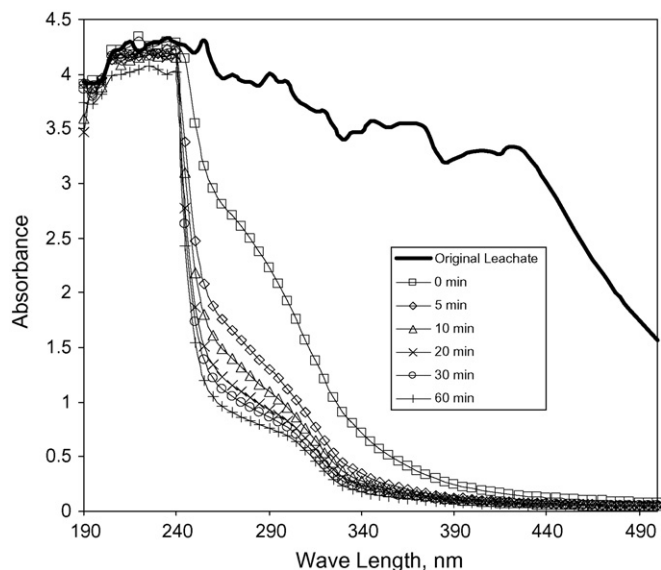

Fig. 2. UV–vis spectrum variation of the original landfill leachate and residual water of leachate after coagulation during ozonation at pH 8.5.

Table 4
Compounds identified in the different extracts[a]

After coagulation	After ozonation
Extract with hexane	
2,2-Dimethylbutane	2,2-Dimethylbutane
2-Methylpentane	2-Methylpentane
Chloroform	Chloroform
Aliphatic hydrocarbons (C_{26}–C_{27})	Aliphatic hydrocarbons (C_{26}–C_{27})
	Methylcyclopentane
	Cyclohexane
Extract with benzene	
6-Methylpyrene	ND
Methylcyclohexane	Methylcyclohexane
Norborane	ND
Toluene	ND
Extract with chloroform–methanol	
Hydroxypropionic acid	ND
Di-p-oxyrane	Di-p-oxyrane
Diphenyloxyrane	ND

[a] Conditions of the GC analysis: GC–MS, Column SPB-225, 30 m × 0.25 mm; 30 °C 5 min, 6 °C/min, 220 °C 8 min.

2.5. Method of kinetic parameters calculation

To determine the rate constant of ozonation in the case of the leachate complexity composition, a simplified mathematical model [39] is applied. To determine the ozone decomposition degree, the ozone concentration variation in the gas phase at the outlet of the reactor is measured at pH 7 and 8.5. In this particular case, the ozone decomposition degree is <3%. In view of this, we may conclude that the preferable mechanism of reactions was by molecular ozone. Based on the results of the partial identification in the fractions of the landfill leachate (see Table 4), the principal organics are coupled in four groups according their reactivity with ozone:

(1) Fulvic acids (FA) and light fraction of humic acids (LFHA).
(2) Simple acids (SA) and the humic substances ozonation by-products (HSOP).
(3) Aromatic hydrocarbons (ArH).
(4) Aliphatic hydrocarbons (AH).

Then the ozonation rate constants for each group (or "factor-group") of organics (as observed constants) are calculated using the program MATLAB 6.5 realizing the numerical calculations based on the simplified mathematical model which have been used before for the kinetic constants calculation of phenols and their mixture [40,41]. There the simple ozonation with *i*-component mixture at pH 7–8 has been treated. This process may be described using the following kinetic model:

$$\frac{\mathrm{d}}{\mathrm{d}t}C_t^{\mathrm{gas}}$$

$$= \frac{W_{\mathrm{gas}}}{V_{\mathrm{gas}}}\left[(C_0^{\mathrm{gas}} - C_t^{\mathrm{gas}}) - K_{\mathrm{sat}}(Q_{\mathrm{max}} - Q_t) + Q_t\sum_{i=1}^{N}k_i c_t^i\right],$$

$$\frac{\mathrm{d}}{\mathrm{d}t}Q_t = K_{\mathrm{sat}}(Q_{\mathrm{max}} - Q_t) - Q_t\sum_{i=1}^{N}k_i c_t^i,$$

$$\frac{\mathrm{d}}{\mathrm{d}t}c_t^i = -\frac{k_i Q_t c_t^i}{V_{\mathrm{liq}}}, \quad i = \overline{1,N} \tag{1}$$

where C_t^{gas} is the ozone concentration in the gas phase (this is ozone which does not react with organic compounds dissolved in the solvent) (mol/L), Q_t the ozone dissolved in liquid phase (mole), and c_t^i is the organic compound concentration at time t, (mol/L). The parameters, involved in the ozonation model description, have the following physical sense: V_{gas} is the volume of gas phase which is assumed to be constant (L), W_{gas} the gas flow (L/s), K_{sat} the saturation constant (s⁻¹), Q_{max} the maximum of ozone being in the saturated liquid phase under the given conditions (mole), k_i the *i*th rate constant of ozone with the organic compound (L/(mol s)) and V_{liq} is the liquid phase volume (L).

To obtain these estimates we used the so-called, "*switching structure filtering method*" suggested in Ref. [44] to construct a numerical estimation of the ozone concentration variation in the water ($\tilde{Q}_t$) (mole) and the rate constants $\tilde{k}_{i,t}$ (L/(mol s)), based on the "on-line" measurements of two types of data:

- The ozone concentration variation in the gas phase in the outlet of the reactor (C_t^{gas}) (mol/L) (Fig. 3).
- The contaminants decomposition dynamics ($\tilde{c}_t^i$) as the summary-effect (or factor-group concentration) of the organics in each of three fractions of the landfill leachate (Fig. 4).
- Then LS-method (the continuous-time version) was applied to estimate k_i.
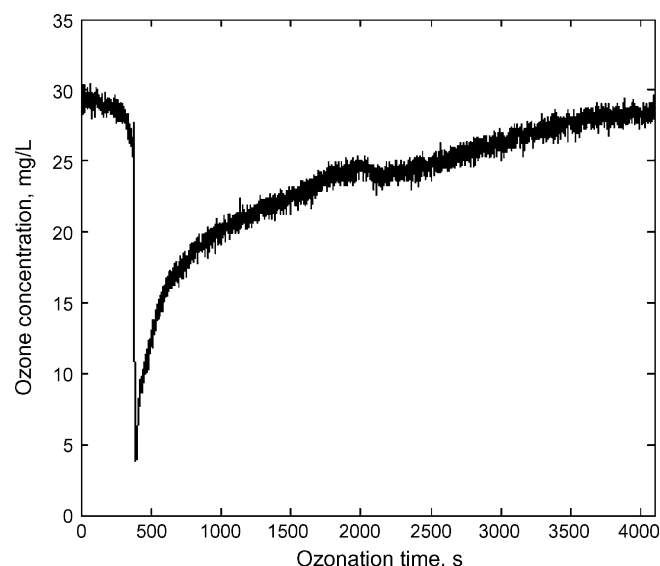

Fig. 3. Variation of the ozone gas phase concentration in landfill leachate ozonation.
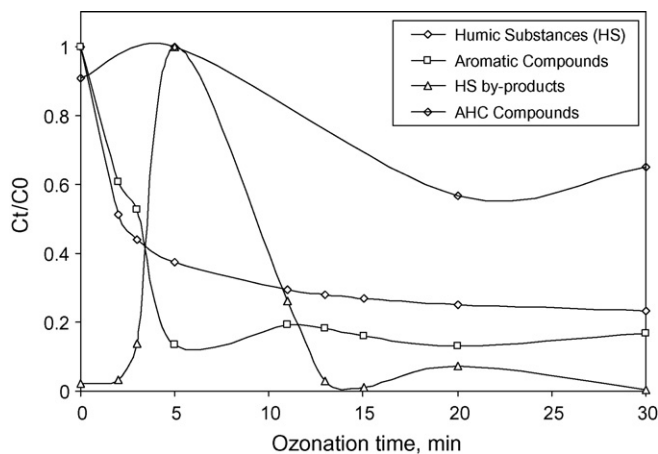
Fig. 4. Decomposition dynamics of organics extracted with benzene and chloroform:methanol; decolorization of initial HS.

3. Results and discussion

3.1. Results of the HPLC analysis

The results obtained by the HPLC technique in the aqueous samples showed the presence of two different compounds with absorbency at 210 nm, which were identified as oxalic and malonic acids. Both were found in the pre-treated sample (oxalic acid 214 mg/L and malonic acid 19 mg/L). As it can be seen from Fig. 5, the oxalic acid is accumulated during the ozonation to 486 mg/L, but the malonic acid concentration does not vary. Forty percent of oxalic acid may be destroyed by ozone with the increasing of the initial pH up to 12.

3.2. Partial identification of same organics with GC/FID and GC/MS techniques

Table 5 represents the principal compounds, identified in this study, in three extracts by the GC/MS technique. As one can see from these data, after ozonation methylcyclopentane and
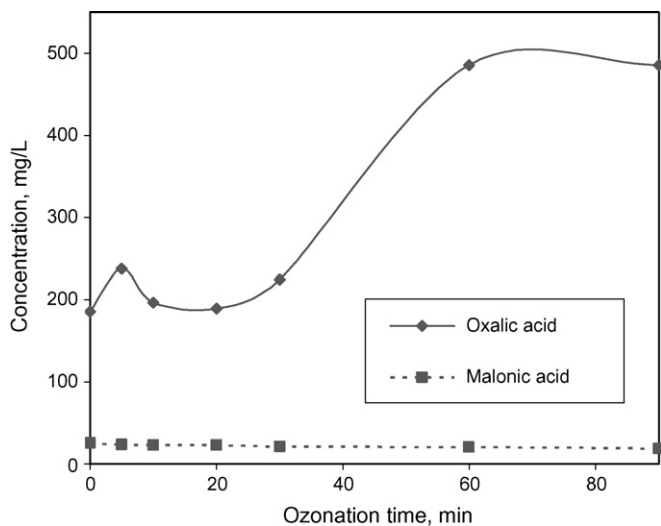

Fig. 5. Concentration variation of oxalic and malonic acids in ozonation.

Table 5
Organic matter distribution in three fractions, 220 °C – 8 min

Fraction	Initial composition (%)
Aromatic	0.4
Chloroform:methanol	71.8
Aliphatic	27.8

cyclohexane were formed in the fraction with hexane. These compounds can be probably interpreted as the fulvic and humic acids ozonation products. The presence of traces of chloroform after coagulation and ozonation may be explained as the effect of extraction with chloroform:methanol. In the fraction with benzene, very toxic compounds such as the derivatives of pyrene and borane were identified [45], but these compounds decomposed completely by ozone. In the polar fraction, the hydroxypropionic acid and diphenyloxyrane were identified, which were also decomposed during the reaction with ozone. Fig. 4 presents the decomposition dynamics of organics in two extracts (with benzene and chloroform:methanol) during ozonation (the results were obtained by the GC/FID technique). These data were obtained due to the summary effect of principal compounds variation in each fraction in ozonation. Furthermore, the decolorization dynamics of HS (the results were obtained by the UV–vis technique) is also presented in the same figure. One can see that the initial HS can be decomposed after 5 min of ozonation as well as aromatic compounds, which decomposed, practically, completely. Then the ozonation by-products at 5 min of ozonation in polar fraction were accumulated, and, finally, all active organics by ozone during 10 min were decomposed. It is important to emphasize that the organic compounds concentration in three extracts was different (see Table 5). So, the maximal organics concentration is in polar fraction (71.8%), and the minimal organics concentration is in aromatic fraction (0.4%). The identification results obtained in this study partially were coincided with results of other authors. So, after the coagulation of the landfill leachate, the presence of different compounds such as aliphatic carboxylic acids, methyl phenols, ethylphenols, alkyl benzenes, aliphatic compounds, amines [8,9,13–17], and light fractions of HS with molecular weight 165–287 [46] were found in residual water. Furthermore, the fragments of proteins, lignin, cellulose, polysaccharides can be contented in water [17,47] too. These compounds may react with ozone at different rate and mechanism and they were decomposed until the formation of the organic acids mixture.

3.3. Decomposition of different groups of organic after coagulation

The main components of the landfill leachate are humic substances (HS) with molecular weight 170–7000 Da [46]. These substances are refractory anionic macromolecules with molecular weight 1000 Da for fulvic acid (FA) and 7000 Da for humic acid (HA). Humic substances consist of alkyl-aromatic units cross-linked mainly by oxygen and nitrogen groups being carboxylic acid, phenolic and alcoholic hydroxyls, and ketone and quinone groups. Fulvic acids are richer in carboxylic acid, phe-

Table 6
Ozonation rate constants for four principal groups of organics

Organics group	Observed constant, k (L/(mol s))
FA and LFHA	3.3×10^5
SA and HSOP	4.6×10^3
ArH	3.8×10^2
AH	3.4

nolic and ketonic groups. The fulvic acids structure is more aliphatic and less aromatic compared to humic acids. The carboxylic functional groups account for 60–90% of all functional groups [48].

The best result of the coagulation treatment is the decreasing of the organic matter content about 70%. This effect was detected by the comparison of the initial and final value of COD (4580 mg/L contrary 1511 mg/L) [42].

After the coagulation of the landfill leachate, the organic substances were separated by extraction with different solvents in order to facilitate the partial compounds identification.

The polar fraction of the pretreated landfill leachate, extracted with chloroform–methanol, contends simple acids (SA) and the mixture of fulvic acids (FA) and light fraction of humic acids (LFHA). These last organics could be destructed completely with ozone at 5 min (decolorization), and by-products of ozonation, also accumulated in the polar fraction, are destroyed at 10 min. The organics extracted with benzene (ArH) were destructed significantly by ozone at 5 min with the intermediates species accumulation also in polar fraction. Finally, the substances extracted with hexane (AH), have a lower ozonation rate and their concentration is not varied during ozonation.

3.4. Estimation of reaction rate constants

Due to the complex leachate composition, it is difficult to elucidate the mechanisms implied in ozonation and the kinetics parameter determination. Using only the measurements "on line" of the ozone concentration variation in the gas phase in the outlet of the reactor (see Fig. 3) and the summary distribution of the organics of four groups of the landfill leachate (see Fig. 4), the observed ozonation constants are calculated for i-component mixture (where "i" is 4) using the program MATLAB 5.3 [41]. The values of the observed constants are presented in Table 6. In view of the obtained results, we may conclude that the FA and LFHA decomposition with height reaction rate ($k = 3.3 \times 10^5$ L/(mol s)) was realized. This process agrees with the leachate decolorization. Next group of organics, which also are reactive with ozone, is by-products of the FA and LFHA decomposition presented also in the polar fraction. These compounds with ozone decompose completely at 10 min ($k = 4.6 \times 10^3$ L/(mol s)). The aromatic compounds degradation was realized enough rapidly at 5 min ($k = 3.8 \times 10^2$ L/(mol s)), since they have a very small concentration in water (0.4%). Aliphatic compounds, extracted with hexane, have low ozonation rate constant ($k = 3.4$ L/(mol s)) and their concentration is not varied significantly in ozonation.

On our opinion, four organics groups, characterized in this study by their reactivity with ozone, may be grouped according to another principle. This depends on the solvents, used for the separation, as well as on an order of the organics extraction. Notice that the proposed method permits to use the same approach for the kinetics study of different landfill leachates.

4. Conclusions

The following conclusions may be done based on the results of this study:

(1) The preliminary extraction of the landfill organics with benzene, chloroform:methanol, and hexane permits separate the organics by its chemical structure in three fractions (aromatic, polar and aliphatic) to simplify the partial identification of organics composition in water.
(2) The toxic compounds formed in ozonation are accumulated in the polar and aromatic fractions since their nature, but these organics are completely destructed at 15 min of ozonation with the formation of the aliphatic carboxylic acids mixture. The last is not toxic and it is much more biodegradable compared to the initial composition.
(3) In the aqueous samples after the coagulation, two compounds are identified: oxalic (214 mg/L) and malonic (19 mg/L) acids; oxalic acid in ozonation is formed and accumulated up to 486 mg/L.
(4) The observed ozonation rate constants estimated for four groups of organics are as follows:
   - $k = 3.3 \times 10^5$ L/(mol s) for FA and LFHA.
   - $k = 4.6 \times 10^3$ L/(mol s) for ozonation by-products (HSOP) and SA.
   - $k = 3.8 \times 10^2$ L/(mol s) for ArH.
   - $k = 3.4$ L/(mol s) for AH.
(5) In particular case, for the studied landfill leachate, the limiting factor of the treatment with ozone is the HSOP decomposition treating more toxic compounds produced in ozonation.

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