

## Research Article

# Landfill Leachates Treatment by $\text{H}_2\text{O}_2/\text{UV}$ , $\text{O}_3/\text{H}_2\text{O}_2$ , Modified Fenton, and Modified Photo-Fenton Methods

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Advanced oxidation processes (AOPs) such as  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , modified Fenton, and modified photo-Fenton processes have been investigated in terms of the treatment of landfill leachate with ratio of  $\text{BOD}_5/\text{COD}$  in the range of 0.22 to 0.24. The modification of Fenton and photo-Fenton processes consisted in the inclusion of precipitation and separation of humic substances at pH 3. Due to the precipitation, the value of COD decreased by 39% and  $\text{BOD}_5$  by 7.1%. The modification of the processes allowed us to improve the efficiency and to decrease the doses of reagents necessary to continue the process. Modified photo-Fenton process proved to be the most effective (92.7% COD removal) of all processes investigated. Additionally, modified-Fenton process was much more effective than the other two processes when compared up to 120 min, while after longer times it gave the least satisfactory results. After 30 min of modified-Fenton process  $\text{BOD}_5/\text{COD}$  ratio increased to 0.43. The parameter referred to as “efficiency of oxidants” was used to estimate the efficiency of all the processes—its value varied from 178 to 239%. Various substances including phthalates, hydrocarbons, silanes, and siloxanes were identified in raw and treated leachate.

## 1. Introduction

In advanced oxidation processes (AOPs) the hydroxyl radical  $\text{HO}^\bullet$  characterized by high redox potential (2,8 V) is produced. The chain reaction evoked by  $\text{HO}^\bullet$  leads to an effective organic pollutants degradation identified by decreased COD value [1]. The use of AOPs in landfill leachate treatment has been the subject of numerous publications, including reviews [1–3]. Despite that it is still difficult to order different methods in terms of their efficiency to oxidize organic compounds. Additionally, the number of studies referring to more than two methods is limited. Another reason is a wide range of concentrations of organics in leachate varying from a few hundreds to more than ten thousand mg/L COD [1]. According to the review published by Kurniawan et al. [1] photo-Fenton and  $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$  processes are the most effective. The efficiency of  $\text{O}_3/\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}_2/\text{UV}$  processes is comparable, while Fenton and  $\text{O}_3/\text{OH}^-$  processes are less effective. In one of the recently published papers [4]  $\text{O}_3/\text{OH}^-$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , and Fenton processes have been compared. It has been shown that Fenton

process yielding 46% COD removal is far less effective than the two remaining processes, in which efficiency is approximately 72%. Primo et al. [5] investigated the efficiency of the treatment of landfill leachate by means of different AOPs. They also classified the methods according to their efficiency in the following order: photo-Fenton, Fenton-like > Fenton >  $\text{H}_2\text{O}_2/\text{UV}$  > UV.

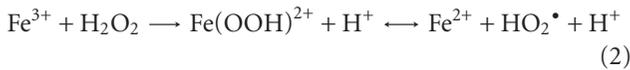
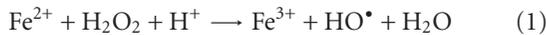
Another interesting method among AOPs is oxone/ $\text{Co}^{2+}$  process. According to the results of the studies carried out by Sun et al. [6] the efficiency of this method is higher than the efficiency of Fenton one. Sulfate radical oxidation process (SR-AOP) [7] is another method worth mentioning. In this method persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) is activated by heating to produce  $\text{SO}_4^{\bullet-}$  radical, which is a strong oxidant ( $E^0 = 2,4 \text{ V}$ ). At pH 4 and  $50^\circ\text{C}$  COD removal is estimated to be 91% and additionally it is possible to remove ammoniacal nitrogen.

Significant differences observed in COD values are caused by different age of landfills. Young landfill leachate shows higher COD values and  $\text{BOD}_5/\text{COD}$  ratio equal to or higher than 0.4, which is typical of domestic wastewaters. Old

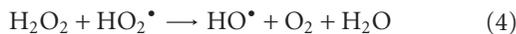
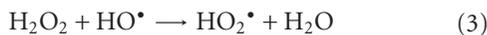
landfill leachate (stabilized) exhibits lower values of COD; its organics are difficult to biodegrade and the BOD<sub>5</sub>/COD ratio is below 0.10. The humic acids with molecular mass between 10 and 100 kDa dominate in old landfill leachate [8]. Additionally, the degree of humification increases with the increasing age of the landfill [9]. Differences in BOD<sub>5</sub>/COD ratio cause different susceptibility of organics to chemical oxidation [1], which leads to a decrease in the concentration of high molecular weight organics (>10 kDa) [10]. Within a certain period of chemical oxidation BOD<sub>5</sub>/COD ratio increases, which results in better biodegradability. Therefore, AOPs are often used as a pretreatment step before a biological process. Fenton process has been the most widely used process of all the AOPs [1, 3]. It is also the most common pretreatment method applied before biological treatment. In contrast, photo-Fenton method is one of the least studied. Fenton process has a few modifications. One of them consists in the separation of the sediment of humic substances precipitating after pH decrease (preliminary coagulation), which is a necessary step in this process. According to the results of our studies [9] sediment formation is an instant process. However, the amount of the sediment increases in time and depends on the pH value: the lower the pH value, the greater amount of the sediment. After the separation of sediment the process is continued.

Fenton process after Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> application continues according to the reactions given below [1].

Initial reactions:



Propagation:



Termination:

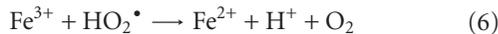
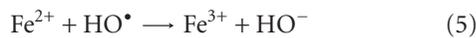
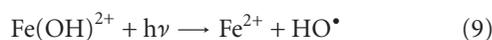
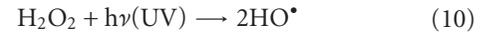


Photo-Fenton process is based on the same reagents as Fenton process but the solution is additionally exposed to UV radiation. As a result, the higher concentration of hydroxyl radicals is obtained. This is due to the fact that ferric complex ion formed in the Fenton reaction ((1), (5)) may be reduced to Fe<sup>2+</sup> by near UV, according to the following reaction in acidic solution [11]:



In the presence of hydrogen peroxide, Fe<sup>2+</sup> can be oxidized according to (1).

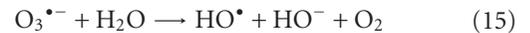
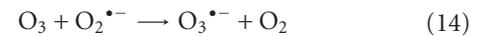
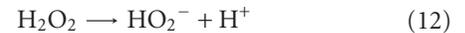
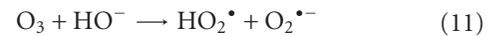
In the H<sub>2</sub>O<sub>2</sub>/UV process HO<sup>•</sup> radicals are generated according to the following reaction:



Additionally, the application of UV light leads to the situation in which organic compounds become more reactive due to the changes in their molecular structure.

Propagation reactions in H<sub>2</sub>O<sub>2</sub>/UV process are exactly the same as in Fenton and photo-Fenton processes ((3), (4)). Termination reaction follows according to (7) and (8).

AOP employing O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> method involves the synergistic action of the two reagents. As a result, hydroxyl radicals are formed according to the following reactions:



Oxidation of organic matter in landfill leachates treated by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> takes place faster than if only one of the above-mentioned oxidants is used. Efficiency expressed as the rate of COD or TOC decrease depends on the ozone dose per mg of COD as well as on the H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ratio. Haapea et al. [12] achieved the highest ratio of TOC decrease for landfill leachates while using ozone dose of 0.5 mg O<sub>3</sub>/mg COD and H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ratio equal to 1:2. Application of other ratios of reagents (1:4 and 3:2) while maintaining the same ozone dose produced less satisfactory results.

The aim of this study was to compare efficiency of four AOPs in leachate treatment—modified Fenton and modified photo-Fenton process (m-Fenton, m-photo-Fenton), as well as H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process. The leachate used in this study can be described as medium stabilized and can be characterized by the values of BOD<sub>5</sub>/COD in the range of 0.1–0.4. Such type of leachate has not been very often used in the studies reported in the literature. Additionally, the effectiveness of oxidation of anthropogenic nonbiodegradable pollutants present in the leachate was also investigated.

## 2. Methods

The paper was conducted on leachate from a landfill site in Lubna near Warsaw. Before the tests samples were subject to 30 min of preliminary sedimentation to separate easily settleable solids.

*2.1. Analysis of Raw and Treated Landfill Leachate.* The determination of COD, total solids (TS), conductivity, total Kjeldhal nitrogen (TKN), ammonia (N<sub>NH<sub>4</sub></sub>), chlorides (Cl<sup>-</sup>), pH, H<sub>2</sub>O<sub>2</sub>, and alkalinity was carried out according to the European Standards. BOD<sub>5</sub> was determined using Selutec

TABLE 1: Characteristics of leachate.

Parameter	pH (—)	Conductivity ( $\mu$ S/cm)	Chlorides (mg/L)	Ammonia (mg/L)	TKN (mg/L)	COD (mg/L)	BOD <sub>5</sub> (mg/L)	BOD <sub>5</sub> /COD (—)
Minimum value	7.8	17600	2400	160	700	4960	1080	0.22
Maximum value	8.7	23000	4000	480	940	6100	1486	0.24
Average	—	20443	2951	339	797	5678	1315	0.23

BSBdigiO<sub>2</sub> respirometer. H<sub>2</sub>O<sub>2</sub> was determined by iodometric method. The analysis of raw and treated landfill leachate was also carried out using GC/MS (Finnigan GCQ Mat). The 1L sample was extracted three times using hexane. Collected organic fractions were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated using Heidolph VV-micro vacuum rotary evaporator. In the next step, the evaporated extract passed through glass column filled with silica gel. The purified extract was evaporated to the volume of 2 mL using the Kuderna-Danish apparatus (Supelco) and analyzed. Separation was achieved using an RTX-5MS Restek Corporation column of 60 m length  $\times$  0.32 mm i.d.  $\times$  0.25  $\mu$ m film thickness. The GC operated at an injector temperature of 280°C with an initial column temperature of 60°C held for 3 min. The temperature was programmed to step up with the speed of 3°C/min until it reached 300°C, which was held for 5 min. The mass spectrometer operated in EI (70 eV) full scan mode, with ion source temperature of 185°C. Mass spectra were compared to the NIST 98.L published spectra. Xcalibur Qual Browser v.1.2 was used for data acquisition and handling.

For sediment precipitated at pH 3.0 and leachate after 0, 5, 10, 15, and 30 min of Fenton reaction, GC-MS analysis was also performed. The separated sediment was then chemically dried by adding small amounts of anhydrous MgSO<sub>4</sub>. In the next step the extraction with dichloromethane in Soxhlet apparatus was carried out. The extract was then evaporated in rotary evaporator using *n*-hexane as a solvent to obtain the volume of 5 cm<sup>3</sup>. Subsequently, it was cleaned up in a column with florisil. Further GC/MS analysis was carried out in the same conditions as the ones used to analyze raw leachate.

**2.2. Experiment.** M-photo-Fenton process was conducted in 1 L glass cylindrical Heraeus Noblelight photoreactor equipped with a cooling jacket. UV radiation in m-photo-Fenton method was provided by a medium-pressure mercury lamp TQ (150 W), immersed in the sleeve. H<sub>2</sub>O<sub>2</sub>/UV process was carried out in 1 L Heraeus Noblelight with low-pressure mercury lamp (15 W). The leachate was stirred with a magnetic stirrer. In O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> method a self-constructed 1 L cylindrical Plexiglas reactor with the diameter of 8 cm was used along with Sander ozone generator. Ozone was introduced through a porous-fritted diffuser, with the dosage of 500–1000 mg/h. M-Fenton process was carried out in 2 L cylindrical reactor equipped with a magnetic stirrer.

After acidifying with 1 M H<sub>2</sub>SO<sub>4</sub> to pH 3.0, the leachate became turbid and humic substances started to precipitate. Full clarification was obtained after 5 h and then the sediment was separated. This process is referred to as a preliminary coagulation. When the separation of the sediment

had been finished, 35% H<sub>2</sub>O<sub>2</sub> and 10% FeSO<sub>4</sub> solutions were added and m-Fenton and m-photo-Fenton processes were continued. After a certain reaction period the leachate was neutralized with 10% NaOH and after 30 min of flocculation and sedimentation the supernatant was examined.

During 5 h of sedimentation of raw leachate some fine solids precipitated. Therefore, H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatments were also preceded by 5 h of sedimentation in order to enable better comparison of all results.

After reaction periods of 0, 15, 30, 60, 120, 240, and 360 min, COD, BOD<sub>5</sub> (only in m-Fenton process), pH, and H<sub>2</sub>O<sub>2</sub> concentrations were determined. Before COD analysis, the remaining H<sub>2</sub>O<sub>2</sub> was removed with catalase. All tests were conducted for 6 different samples of leachate and the results were calculated to obtain average values.

### 3. Results and Discussion

**3.1. Raw Leachates.** The composition characteristic of the landfill leachates is given in Table 1. It can be noticed that the leachates are rich in organic substances (COD 4960–6100 mg/L), ammonium ions, and chlorides. Due to the fact that the leachates come from an old, medium-stabilized landfill site, they have BOD<sub>5</sub>/COD values of 0.22–0.24. Since this ratio is far below 0.4, the leachates can be classified as refractory to biological treatment.

#### 3.2. AOPs Results

**3.2.1. Modified Fenton Process.** Changes of COD during the process are shown in Figure 1. Preliminary coagulation at pH 3.0 and 5 h of sedimentation led to the average decrease in COD by 39.3% (Figure 1, time “0”). COD value was decreasing relatively fast until 60 min. After that the process started to slow down. Figure 1 proves that the optimal effect of treatment was obtained for H<sub>2</sub>O<sub>2</sub>/Fe (II) doses 3500/500 and 3000/1000 mg/L. Application of doses 4000/500 and 4000/1000 resulted in slightly worse effect. For the two optimal doses the value of COD decreased by approximately 75% after preliminary coagulation and 60 min of Fenton reaction. For Fenton reaction periods of 15, 120, 240, and 360 min these values were 53.6, 77.9, 82.2, and 87.5%, respectively. BOD<sub>5</sub> value also decreased during Fenton process. Preliminary coagulation at pH 3.0 led to the increase in BOD<sub>5</sub>/COD ratio to 0.33–0.35. For the above-mentioned optimal doses and after Fenton reaction period of 15 min the ratio increased to 0.42–0.45. After that time the ratio started to decrease, reaching the average values of 0.36, 0.33, 0.30, and 0.26 after 30, 60, 120, and 480 min of reaction,

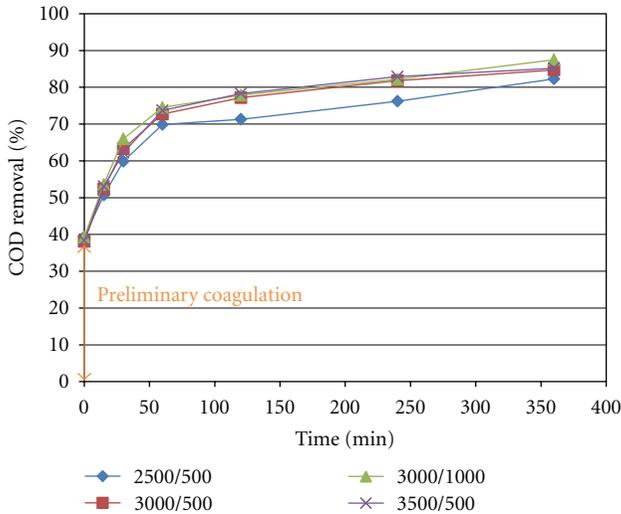


FIGURE 1: COD removal as a function of time for m-Fenton process and different doses of  $H_2O_2/Fe$  (II).

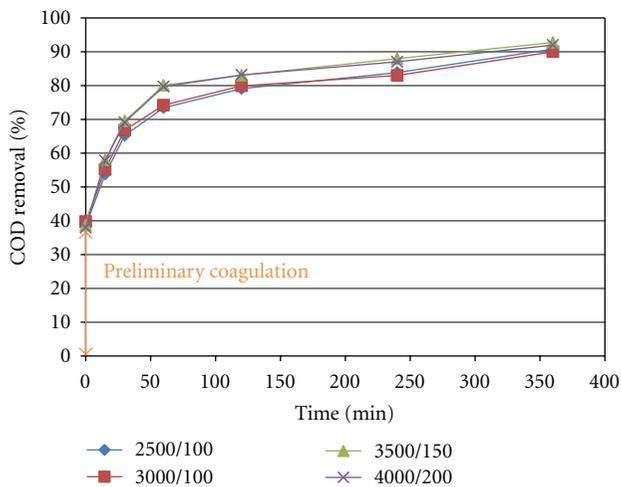


FIGURE 2: COD removal as a function of time for m-photo-Fenton process and different doses of  $H_2O_2/Fe$  (II).

respectively. The same ratio was obtained after 20 min if smaller reagent doses were used (2500/500).

**3.2.2. Modified Photo-Fenton Process.** Changes of COD during the process are shown in Figure 2. Similarly to m-Fenton process, a fast drop of COD occurred until 60 min. After that the process started to slow down. Optimal dose of  $H_2O_2/Fe$  (II) was estimated to be 3500/150 mg/L. After reaction periods of 60, 120, 240, and 360 min, COD value decreased by 80.1, 83.0, 88.0, and 92.7%, respectively. Doses of 4000/150 and 4000/200 led to only slightly better results. For doses 4000/100, 4000/150, and 4500/200 (data not shown in the picture to ensure its clarity), the effect was less pronounced. For doses of 3500/100 the effect was a little better than that for 3000/100.

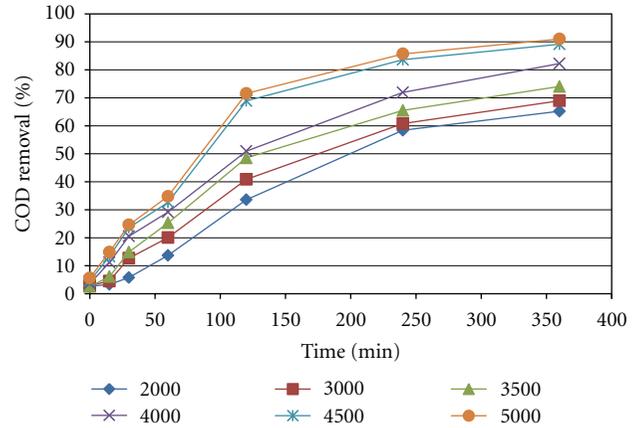


FIGURE 3: COD removal as a function of time for  $H_2O_2/UV$  process and different doses of  $H_2O_2$ .

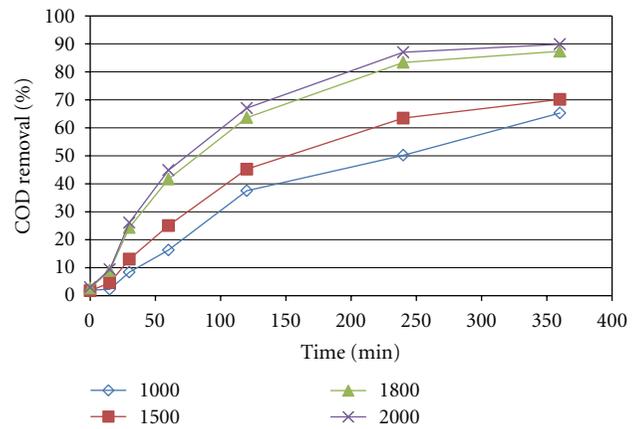
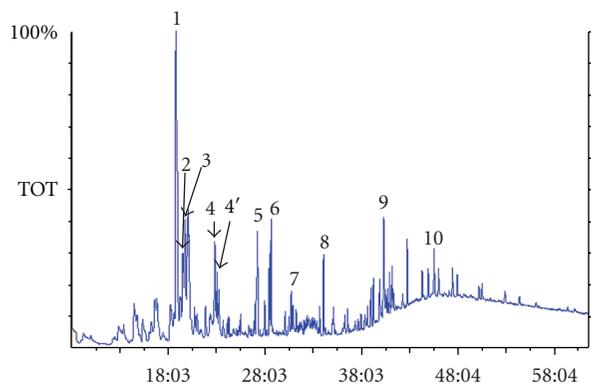


FIGURE 4: COD removal as a function of time for  $O_3/H_2O_2$  process and different doses of  $H_2O_2$ .

**3.2.3.  $H_2O_2/UV$ .** Figure 3 shows changes in COD values for different doses of  $H_2O_2$  (2000–6000 mg/L). Five hours of preliminary sedimentation resulted in 4.6% COD removal. The effect of the process for each sample increased considerably when  $H_2O_2$  dose was increased to 4500 mg/L. Therefore, this dose can be considered as optimal. The resulted decrease in COD after 60, 120, 240, and 360 min was equal to 32.7, 68.9, 83.6, and 89.2%, respectively. The dose of 5000 mg/L slightly improved the process efficiency—91.0% after 360 min. For doses 5500 and 6000 mg/L the efficiency was approximately the same or slightly lower.

**3.2.4.  $O_3/H_2O_2$ .** The COD values for  $H_2O_2$  doses varying from 1000 to 2000 mg/L and  $O_3$  dose of 750 mg/h are shown in Figure 4. The 3.0% of COD removal due to sedimentation was taken into account as above. The efficiency of the process increased when  $H_2O_2$  dose was increased up to 2000 mg/L. For higher doses (to 3000 mg/L) the efficiency was approximately the same. For the dose of 2000 mg/L, considered as optimal, the decrease in COD value after 60, 120, 240, and 360 min was equal to 44.8, 67.1, 87.0, and 89.9%, respectively.



- (1) Bicyclo[2.2.1]heptan-2-one, 5,5,6-trimethyl-
- (2) Cyclopentane, 1-methyl-1-(2-methyl-2-propenyl)-
- (3) Benzenemethanol, 4-trimethyl-
- (4) Phenol, m-tert-butyl-
- (4') Phenol, 2,3,5,6-tetramethyl-
- (5) 3,4-undecadiene-2,10-dione, 6,6-dimethyl-
- (6) o-hydroxybiphenyl
- (7) Benzophenone
- (8) 2-cyclopropen-1-one, 2,3-diphenyl-
- (9) Phenanthrene, 1-methyl-7-(1-methylethyl)-
- (10) Phthalate, di-isooctyl

FIGURE 5: Chromatogram of raw leachate.

Decreasing the  $O_3$  dose to 500 mg/L caused a considerable decrease in the efficiency of the process—COD removal related to 2000 mg/L  $H_2O_2$  was similar to the value obtained for the higher dose of  $O_3$  and 1000 mg/L  $H_2O_2$ . An increase in  $O_3$  dose to 1000 mg/L did not improve the efficiency of the process even when lower doses of  $H_2O_2$  were applied.

**3.3. GC-MS Analysis.** Figure 5 depicts GC-MS chromatograms obtained for raw leachates. Peaks corresponding to the main identified substances are indicated in the figure.

Substances which were either the main pollutants in raw leachates (Figure 5) were detected in leachates treated by AOPs in significantly lower concentrations or were not detected at all. They were oxidized to simple compounds, which cannot be detected by GC/MS method. Due to the matrix complexity it is impossible to derive the sample and unequivocally identify the products of the oxidation. Simple compounds present in raw leachates were removed and have not been detected either in treated leachates or in the resulting sediment. The major identified compound in treated leachates was di-n-butyl phthalate. Similar amounts of this compound were identified both in sediment after preliminary coagulation at pH 3.0 and in remaining leachate. A small part of the total amount of the compound was oxidized—after 30 min 70% of di-n-butyl phthalate remained in leachate. Moreover, the presence of aliphatic hydrocarbons C26-C40 was reported, 70–80% of which precipitated at pH 3. The remaining amount was oxidized in 90% after 30 min. The list of compounds detected in the greatest amount in raw and treated leachates is given in Table 2. The table also includes the degree of the decrease in

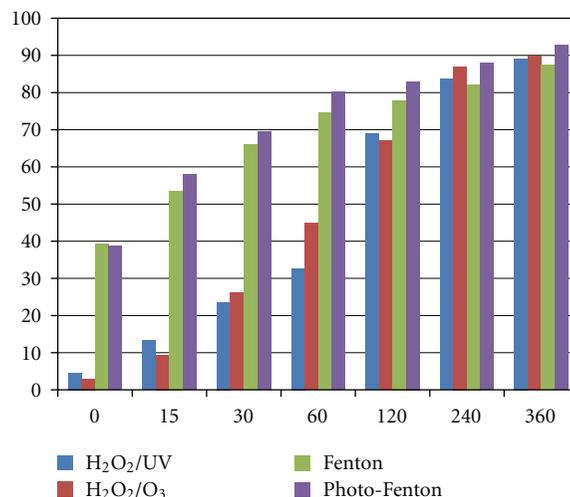


FIGURE 6: COD removal as a function of time for all process.

the compounds' content after preliminary coagulation and Fenton process.

Additionally, small amount of the following substances has been detected in raw leachates:

- (i) tricosanoic acid methyl ester and dodecanoic acid methyl ester,
- (ii) hasuban-9-ol, 7,8-didehydro-4,5-epoxy-3-methoxy-17-methyl (5- $\alpha$ ),
- (iii) benzene, 1-chloro-3,5-bis(1,1-dimethylethyl)-2-(2-propenyloxy),
- (iv) diazene, diphenyl-[E],
- (v) cyclopentasiloxane, decamethyl,
- (vi) hexa-T-butylthiatriisiletane.

## 4. Discussion

Figure 6 presents the efficiency of the treatment using the four methods described in this study, for the doses of reagents considered as optimal. For the process periods up to 120 min the methods can be ordered with respect to their oxidation efficiency as follows: m-photo-Fenton > m-Fenton >  $H_2O_2/UV \sim O_3/H_2O_2$ . After reaction period of 360 min the highest COD removal was obtained for m-photo-Fenton method and the lowest for m-Fenton method. However, the values after this period did not vary significantly. For short reaction periods the prevalence of m-Fenton and m-photo-Fenton methods is evident. It results from considerable COD removal obtained in coagulation at pH 3, which preceded the Fenton reaction. This advantage is observed until 60 min of the process. With the progress of m-Fenton and m-photo-Fenton processes, the contribution from the preliminary coagulation at pH 3.0 to the overall effect of the processes decreases. Preliminary coagulation does not completely eliminate the contribution from the final coagulation to COD removal. This contribution is significantly smaller and decreases with the increasing time of the process duration

TABLE 2: Main compounds detected in raw leachates and after Fenton process and the corresponding degree of removal.

Compounds	Preliminary coagulation (%)	Fenton (15 min) (%)	Fenton (30 min) (%)
Bicyclo[2.2.1]heptan-2-one, 5,5,6-trimethyl-	61	99	n.d.
Cyclopentane, 1-methyl-1-(2-methyl-2-propenyl)-	66	99	n.d.
Benzenemethanol, 4-trimethyl-	53	n.d.	n.d.
Phenol, m-tert-butyl-	45	n.d.	n.d.
Phenol, 2,3,5,6-tetramethyl-	45	n.d.	n.d.
3,4-undecadiene-2,10-dione, 6,6-dimethyl-	50	n.d.	n.d.
<i>o</i> -Hydroxybiphenyl	55	n.d.	n.d.
Benzophenone	50	n.d.	n.d.
2-Cyclopropen-1-one, 2,3-diphenyl-	64	n.d.	n.d.
Phenanthrene, 1-methyl-7-(1-methylethyl)-	81	n.d.	n.d.
Phthalate, di-butyl	26	30	30
Phthalate, di-isooctyl	50	56	60
Aliphatic hydrocarbons C26–C40	70–80	90–95	n.d.
2,4,6 (1H,3H,5H)-pyrimidinetrione, 5-ethyl-5-(3-methylbutyl)-1,3-bis(trimethylsilyl)	80–90	95	n.d.
1,3,5,7,9-Penthaethylbicyclo[5, 3, 1] pentasiloxane	50	70	90
Benzeneacetic acid, alpha,3,4-tris[(trimethylsilyl)oxy]-methyl ester	90	n.d.	n.d.
Ent-3a,10-dihydroxy-13-iodomethyl-16-oxo-8,13-epi-17,20-dinogibberell-1	90	n.d.	n.d.
3,4-Dihydroxymandelic acid, ethyl ester, tri-TMS	89	97	98
2H-1,4-Benzodiazepin-2-one, 7-chloro-1,3-dihydro-5-phenyl-1-(trimethylsilyl)	50	n.d.	n.d.

[9]. At the same time, after 60 min of the process the rate of Fenton reaction clearly decreases. This decrease in the reaction rate can be explained by the inhibition of Fe (II) ions generation, according to the reactions (2) and (6). Much higher rate of  $H_2O_2/UV$  and  $O_3/H_2O_2$  processes compared to Fenton reaction results not only from greater production of  $OH^\bullet$  radicals but also from higher organics' concentration. Very high and similar values of COD removal (87.5–92.7%) for all processes after 360 min (Figure 6) show that products of the final oxidation are also similar and resistant to further oxidation by  $OH^\bullet$  radicals.

We have recently showed [9] that the modification of photo-Fenton process results in the higher increase in the efficiency compared to the classic process than in case of the modification of Fenton process. This observation and high photo-Fenton reaction rate caused by the regeneration of  $OH^\bullet$  radicals (9) lead to very high value of COD removal (92.7%) obtained in this study.

Results of comparative studies conducted by other researchers [1, 13] proved that the efficiency of Fenton process is lower than the efficiency of  $H_2O_2/UV$  and  $O_3/H_2O_2$  processes. Only Primo et al. [5] reported that Fenton process was more effective than  $H_2O_2/UV$  process. Higher efficiency of m-Fenton process obtained in this study for shorter reaction periods proves the need for conducting such research in the modified way, including coagulation at pH 3.0, separation of the precipitate, and continuation of the process by adding other reagents. Precipitation of humic substances at pH 2.0–4.0 was studied by Rivas et al. [8]. The obtained value of COD removal was equal to

25%. After separating the precipitate, the next stages of the process included coagulation with  $FeCl_3$  at pH 3.5 and finally Fenton reaction. Overall COD removal was nearly 90%. Other researchers who studied Fenton reaction did not consider coagulation of humic substances. There is one more advantage of initial coagulation. As a result, Fenton reaction itself is conducted in leachate with much lower COD value, which requires lower reagents doses.

Schulte et al. [13] conducted similar research with stabilized leachate (COD 780 mg/L) using the same three processes, apart from photo-Fenton process. It was shown that Fenton process allowed reducing COD only by 60%.  $H_2O_2/UV$  process gave the result of 90% reduction and  $O_3/H_2O_2$  was only slightly more effective. The results of our paper on modified Fenton process can be compared to the research of Lopez et al. [14]. They gained similar results during the treatment of leachate and obtained similar COD/BOD<sub>5</sub> ratio 10540/2300 (4.6) for  $H_2O_2/Fe(II)$  doses of 1000/830 mg/L—COD removal was equal to 60%. The presented results are similar to those of Calli et al. [15]. For not stabilized leachate with COD/BOD<sub>5</sub> ratio equal to 5850/2860, it was possible to obtain COD removal by 87%. Similar efficiency was gained by Zhang et al. [16, 17]—approximately 70 and 89% COD removal. Lower value of COD removal for stabilized leachate (61%) was reported by Deng [18].

The results obtained for modified photo-Fenton process were much better than the ones obtained by other researchers in “classic” photo-Fenton process and better than ever obtained for any AOPs [1]. de Morais and Zamora [19] achieved 58% of COD removal for leachate having similar

values of COD and BOD<sub>5</sub>. Kim et al. [11] while studying stabilized leachate (COD/BOD<sub>5</sub> 1150/5) reported the value of COD removal equal to 70%. In this study the used H<sub>2</sub>O<sub>2</sub> dose was similar to COD value and mass ratio of H<sub>2</sub>O<sub>2</sub>/Fe (II) was approximately 15.

The results shown in Figure 6 do not explicitly point out which method is more effective—H<sub>2</sub>O<sub>2</sub>/UV or O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>. The advantage of one method over the other is very small and the difference in the efficiency of the two methods is within the experimental error. The efficiency obtained in this study is similar to that reported by Schulte et al. [13] and Steensen [20], who also achieved COD removal by 90% for stabilized leachate with COD value of 1200 mg/L. de Moraes and Zamora [19] obtained the value of 56%, Ince [21] 54%, and Shu et al. [22] 65% of COD removal. The results obtained by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> method were also similar to the results published by Schulte et al. [13] and much higher than those of Haapea et al. [12], who reported only 50% COD removal.

In order to estimate the efficiency of Fenton process, a parameter referred to as “efficiency of hydrogen peroxide” was recommended by Kang and Hwang [23]. However, we suggest some modifications of this parameter. The parameter referred to as “efficiency of oxidants” will allow one to estimate the efficiency of both oxidants,

$$\eta(\%) = \frac{\Delta\text{COD}}{0.4706 \cdot [\text{H}_2\text{O}_2] + 0.333 \cdot [\text{O}_3]} \cdot 100\%, \quad (16)$$

where  $\Delta\text{COD}$ —COD removed, mg/L,  $[\text{H}_2\text{O}_2]$ ,  $[\text{O}_3]$ —doses of H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, mg/L,

0.4706- factor—COD theoretically removed (mg) by 1 mg H<sub>2</sub>O<sub>2</sub>,

0.333- factor—COD theoretically removed (mg) by 1 mg O<sub>3</sub>.

The values of this parameter for particular processes, without taking into account the results of sedimentation and coagulation at pH 3, for reagent doses considered as optimal, were equal to 184.6%, 239.8%, 178.3%, and 238.0% for H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, m-Fenton, and m-photo-Fenton processed, respectively. Very high values of this parameter prove that the role of oxygen is significant in oxidation processes, since it reacts with organic radicals generated in the reaction of organic compounds with hydroxyl radical and later reactions [1].



The organic radical (R<sup>•</sup>) reacts with oxygen to yield peroxy radical (RO<sub>2</sub><sup>•</sup>), which initiates subsequent chain and oxidation reactions.

It is worth noticing that after 360 min of the process several dozen mg/L of H<sub>2</sub>O<sub>2</sub> still remains in the leachate (the amount which has not reacted). Moreover, 30% of ozone leaves the reaction environment and some oxidants are lost during the processes. Therefore, the role of oxygen in oxidation process may be even twice higher than the participation of OH<sup>•</sup> radicals.

It should be also noted that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process is characterized by the high efficiency of oxidants, which is much higher than in H<sub>2</sub>O<sub>2</sub>/UV process. In the same time, the efficiency of COD removal is similar for the two processes. Additionally, it is also comparable to the value typical for a more effective m-photo-Fenton process. In O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process the dose of H<sub>2</sub>O<sub>2</sub> is more than twice lower than in case of H<sub>2</sub>O<sub>2</sub>/UV process. In the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process much higher contribution of oxygen into the oxidation results from its high dose supplied together with ozone and from its in situ generation, according to the reaction (13). In the H<sub>2</sub>O<sub>2</sub>/UV process conducted in the photoreactor, the oxygen is supplied in much smaller quantities. Additionally, H<sub>2</sub>O<sub>2</sub>/UV process is more sensitive to the scavenging effect of H<sub>2</sub>O<sub>2</sub> [1]. Due to this effect, high H<sub>2</sub>O<sub>2</sub> concentration slows down the oxidation rate, while at low H<sub>2</sub>O<sub>2</sub> concentration the generation of HO<sup>•</sup> radicals is insufficient.

The results of GC-MS analysis are also interesting. The presence of hydrocarbons and phthalates was expected. O-phthalic acid diesters have been detected in many landfill leachates [24]. They are widely used in many materials (PVC, other resins, paints, adhesives), which after their service life are landfilled. However, the presence of silicon derivatives silyl ethers, siloxanes, silanes, and siletanes was unexpected. Similarly to phthalates, they are also used as plastic additives, in cosmetics, defoamers, soaps, deodorants, lubricants, and other materials. Most of organics detected in landfill leachates in our studies were not reported by other researches. Most of them are probably the products of the conversions taking place in the landfill.

*4.1. Kinetics of m-Fenton and m-photo-Fenton Process.* The reaction rate of Fenton process causes problems in its description. In order to describe the process of Fenton kinetics pseudofirst and second order equations were employed by Wu et al. [25]. Godala and Nowicki [26] used a fractional-order equation to describe dihydroxyphenols oxidation kinetics in relation to the concentration of oxidized substances and H<sub>2</sub>O<sub>2</sub>. Wu et al. [25] recognized that Fenton process kinetics cannot be described by a simple equation and suggested an elaborated model, considering reaction rate constants for the ones described by (1)–(8). The same authors [27] suggested a two-stage model consisting of a “rapid reaction stage” followed by a “stagnant stage” for leachate. An attempt to apply these models in this study did not give satisfactory results. The process seems to be too complex and assumptions taken by other authors do not consider factors such as coagulation or reaction of organic radicals with oxygen. Reference [9] revealed that an empirical model can be successfully employed to describe Fenton reaction rate as a change of COD values in time according to the following equation:

$$\frac{d[\text{COD}]}{dt} = -at^m[\text{COD}], \quad (19)$$

where “*t*” time and “*a*” and “*m*” constants are dependent on the initial concentration of reagents.

TABLE 3: The values of the constants and correlation coefficients for m-Fenton and m-photo-Fenton processes.

	$a \cdot 10^{-2}$ (—)	$-m$ (—)	$R^2$ (—)
m-Fenton 2500/500	3.36	0.496	0.920
m-Fenton 3000/500	4.20	0.503	0.927
m-Fenton 3000/1000	4.48	0.503	0.919
m-Fenton 3500/500	4.23	0.494	0.933
m-photo-Fenton 2500/100	4.03	0.430	0.966
m-photo-Fenton 3000/100	4.18	0.436	0.940
m-photo-Fenton 3500/150	5.41	0.456	0.948
m-photo-Fenton 4000/200	4.84	0.4506	0.963

After integration and applying double logarithm the following formula is obtained:

$$\ln \ln \frac{[\text{COD}]_0}{[\text{COD}]} = n \ln t + \ln k, \quad (20)$$

where  $[\text{COD}]_0$  initial COD,  $n = m + 1$ ,  $k = a/n$ .

In the present study the same empirical model has been used to describe m-Fenton and m-photo-Fenton processes involving oxidation reactions as well as final coagulation and sedimentation. High values of correlation coefficient (from 0.919 to 0.966) prove that the above-mentioned equation may be successfully used to describe the kinetics of the decrease in COD value in m-Fenton and m-photo-Fenton processes. The values of the constants and correlation coefficients for the processes determined in relation to the reagent dose have been included in Table 3.

Constant “ $a$ ” has the highest values for the individual processes when the reagent dose is optimal. Comparing the values of “ $m$ ” constant, which is the exponent in the equation, it can be stated that the decrease rate in COD value during m-photo-Fenton process depends on time to the higher extent than in case of m-Fenton process.

## 5. Conclusions

Adjusting pH to 3.0, which is a necessary step to conduct m-Fenton process, leads to a slow precipitation of humic substances. However, the separation of the sediment before adding next reagents significantly decreases both COD value and COD/BOD<sub>5</sub> ratio. The continuation of m-Fenton or m-photo-Fenton processes results in higher COD removal and the values obtained in the studied leachate correspond to 87.5% and 92.7%, respectively. The reported efficiency of 120 min of m-Fenton process was higher than the efficiency obtained for either O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/UV processes, for which the values of efficiency were similar. After longer reaction periods the value of the efficiency of m-Fenton process was slightly lower than values observed for the other two processes. Based on the obtained results, it can be stated that m-photo-Fenton process was definitely the most effective of the all processes studied, regardless of the reaction period. Additionally, the “efficiency of oxidants” parameter is recommended to be used to assess the efficiency of AOPs. Its

value allows to estimate the approximate amount of oxygen used in the oxidation process.

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