

## Pretreatment of Stabilized Landfill Leachate Using Ozone

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### ABSTRACT

The paper presents the possibility of using the ozonation process in landfill leachate pretreatment. The study was conducted in three stages. In the first stage, the landfill leachate was subjected only to the ozone, with the dose varying from 10 mg/dm<sup>3</sup> to 40 mg/dm<sup>3</sup>. As part of this stage of research, the effect of changes in the pH of wastewater undergoing the process of ozonation on the efficiency of TOC removal was examined. For all the tested pH values (pH = 3.5, pH = 7 pH = 8.5 pH = 10), the TOC removal rate constant ( $k_{Rowo}$ ) during ozonation was determined. In the second stage of the study, the ozonation process was facilitated by UV radiation. Additionally in this stage, the rate of generation of OH• radicals was accelerated by the addition of hydrogen peroxide to the reactor. The COD:H<sub>2</sub>O<sub>2</sub> ratio by weight was 1:2.5, 1:5 and 1:10 and 1:20. In the last stage of the study, we attempted to assist the ozonation process using ultrasonic field. The employed vibration amplitude amounted to 25 μm and sonication time equalled 300 seconds. It was found that the ozonation process is the most effective at alkaline pH (8.5). The TOC removal efficiency was 37% (346 mg/dm<sup>3</sup>) after 60 minutes of ozonation. The best results of pollutants oxidation measured as COD and TOC removal were observed when the dose of ozone was 20 mg/dm<sup>3</sup>. The combination of sonication and ozonation has resulted in a reduction of COD and TOC values by 370 mg/dm<sup>3</sup> and 126 mg/dm<sup>3</sup>, respectively, in comparison to the ozonation process alone. It was found that the most effective process in landfill leachate treatment is the combination of ozonation with hydrogen peroxide addition (COD:H<sub>2</sub>O<sub>2</sub>=1:10). The COD, TOC and BOD values were 65%, 62% and 36% lower, respectively, in comparison to ozonation process conducted alone.

**Keywords:** landfill leachate, ozonation, hydrogen peroxide, ultrasonic field, advanced oxidation process

### INTRODUCTION

The term ‘leachate’ means the water generated in landfills due to the seepage of rainwater through the bed. They elute organic and mineral compounds resulting from the biological and physicochemical changes from the landfills waste. Although many methods may be applied, the most appropriate leachate treatment choice will depend on its features, technical applicability, cost effectiveness, and other factors related to the quality requirements of the effluents. The leachate produced in mature landfills contains significant amounts of humic acids having a very stable structure which is difficult to breach by bacteria. Therefore, the purification efficiency by the biological method of the activated sludge is not very high [Kurniwana and Wai-hung 2006;

Kwarciak-Kozłowska and Sławik-Dembiczak 2016]. Advanced oxidation processes (AOP) represent relatively new methods while their mechanism is based on the generation of free hydroxyl radicals. AOP encompasses ozonation which is a treatment based on the high oxidant power of ozone that can be used to decompose large organic molecules into smaller and less complex ones occurring at normal pressure and temperature being, hence, industrially interesting [Amaral-Silva et al. 2016]. Ozone belongs to very strong oxidants and therefore starts reactions with many organic and inorganic compounds. It is selective in direct reactions with organic compounds; Conversely, hydroxyl radicals are usually non-selective with respect to these compounds [Zarzycki 2002]. Ozonation alters the molecular structure of refractory organic compounds pres-

ent in the leachate, turning them into compounds that are easily assimilated biologically. The ozone processes can be made more effective for example at high pH ( $O_3/OH^-$ ) and by the addition of hydrogen peroxide ( $O_3/H_2O_2$ ). These systems (Peroxone process) favour the production of hydroxyl radicals ( $\cdot OH$ ), which are highly reactive species.  $OH^-$  and  $H_2O_2$  initiate a series of radical reactions that enhance the ozone decomposition to yield  $\cdot OH$  [Bila et al. 2005; Tizaoui et al. 2007, Catalkaya and Kargi 2007; Hansen et al. 2016; Liu et al. 2015; Zarzycki 2002]. Furthermore, the effect of the ultrasonic wave is connected with the stimulation of the cavitation phenomenon [Suslick 1989]. The energy released during the implosion of the cavity bubbles is able to initiate a thermal decomposition of water particles using the hydroxyl radicals [Barbusiński 2013; Cesaro et al. 2013; Xu et al. 2005].

As a result, this research was carried out in order to investigate the treatment of landfill leachate using ozone-bases processes (i.e.  $O_3$  alone,  $O_3/H_2O_2$  and  $O_3/US$ ). This study investigated the effects of different operating parameters such as,  $H_2O_2$  concentration (COD:  $H_2O_2$  was 1:2.5, 1:5 and 1:10 and 1:20), dose of ozone (10–40 mg/dm<sup>3</sup>) and sonication process (amplitude 25 µm, sonication time 300).

## MATERIALS AND METHODS

The leachate was derived from the regional municipal waste landfill in Silesian Province (Poland). The leachate was characterised by the pH of 7.89 and light brown colour. The COD value was 2885 mg/dm<sup>3</sup> on average and BOD was under 190 mg/dm<sup>3</sup>. The BOD/COD ratio was at a low level (0.06) that indicated low biodegradability. The amount of TOC was 550 mg/dm<sup>3</sup>.

The process of landfill leachate ozonation was performed in a cylindrical glass reactor with the diameter of 10 cm and active volume of 4 dm<sup>3</sup>. The positive pressure system for supplying of air-ozone mixture to the reaction chamber was used. Fine-bubble aeration was performed using the diffuser located at the reactor bottom. Ozone was generated from oxygen using the OZOMATIC LAB 802 ozonizer, with the range of air-ozone mixture production ranging from 0.1 to 1 dm<sup>3</sup>/min. The gas flow rates were adjusted using the RO6 RP T96193 rotameter (max 45 dm<sup>3</sup>/h). The measurement of the ozone content at the out-

let from the reaction chamber was conducted using the Dreschel washing bottle with the absorption solution connected with the valve located at its top [Kwarciak-Kozłowska et al. 2016].

The sonication of the landfill leachate was performed using the Sonics vibro cell ultrasonic disintegrator which generated the ultrasonic wave with vibration frequency 40 kHz. The power adjustment in the device was possible through the digital adjustment of the percentage of maximal amplitude of the sonotrode (max 123 µm) [Kwarciak-Kozłowska and Sławik-Dembiczak 2016].

The examinations were performed at three stages. At the first stage, the leachate was exposed to the effect of ozone, with the doses changing in the range from 10 mg/dm<sup>3</sup> to 40 mg/dm<sup>3</sup>. The ozone efficiency was controlled by the adjustment of the generator efficiency (from 5% to 100%) to the specific gas flow rate (from 10 dm<sup>3</sup>/h to 40 dm<sup>3</sup>/h). At this stage, the effect of pH of the liquors subjected to ozonation on the degree and rate of TOC removal was determined.

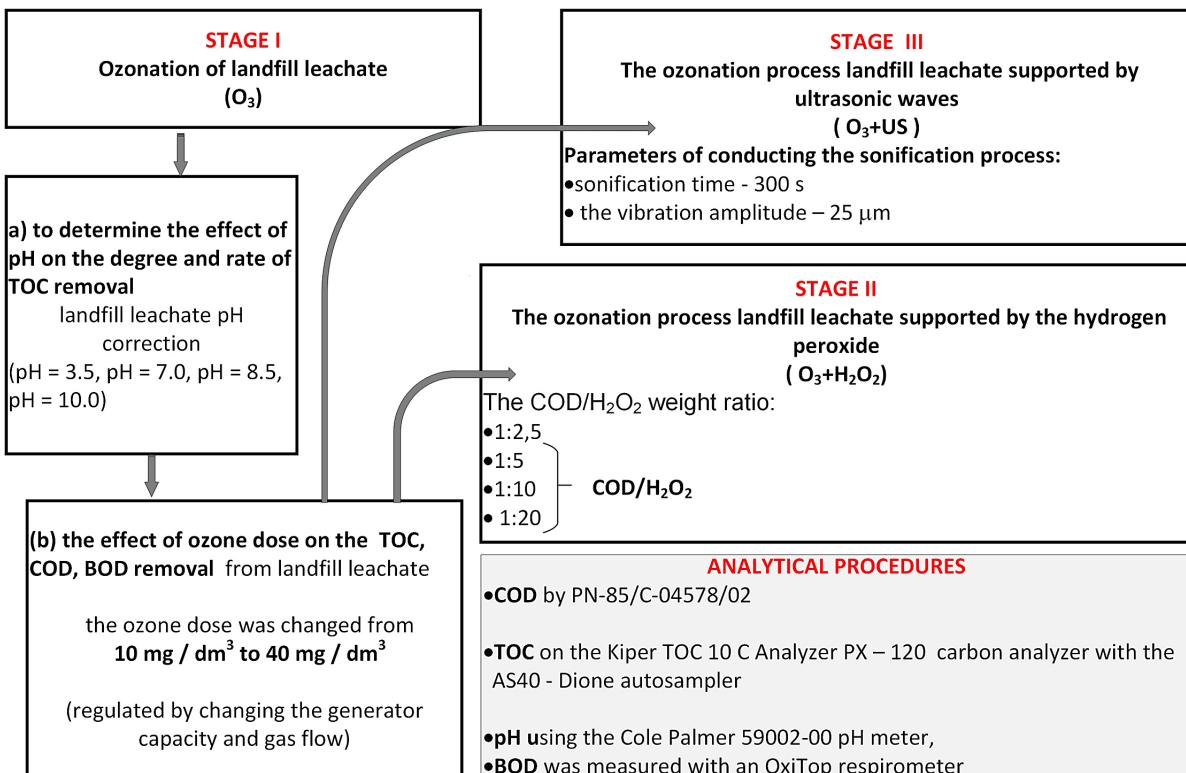
At the second stage of the examinations, the rate of generation of  $OH\cdot$  radicals in the ozonation process was accelerated by adding hydrogen peroxide to the reaction chamber. Its amount was increased in the geometrical progress by q=2, at initial amount of 1:2.5 (ChZT: $H_2O_2$ ).

At the last stage, the ozonation process was combined with the ultrasonic field. The ultrasonic field parameters such as sonication time (300 sec) and vibration amplitude (25 µm) used at this stage were the most advantageous values determined from the previous examinations concerning demonstration of the effect of the ultrasonic field on the change of the biodegradability of landfill leachate [Kwarciak-Kozłowska and Sławik-Dembiczak 2016]. The efficiency of the unit processes used in the study was controlled based on the changes in the levels of COD, TOC and BOD. The study design and methodology of determination are presented in Figure 1.

## RESULTS AND DISCUSSION

### Effect of pH of landfill leachate and ozone doze on the degree of ozonation of contaminants (stages 1)

The first step of the experiment examined the effect of the initial pH value of the landfill leachate subjected to ozonation on the TOC removal



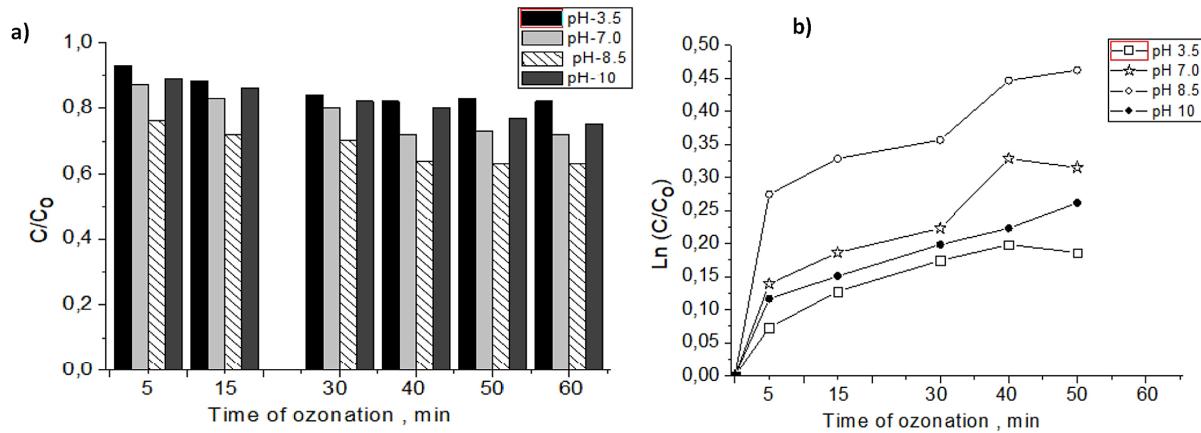
**Figure 1.** The scheme of treatment the landfill leachate in ozonation process

rate. This stage was performed at a constant ozone dose of 10 mg/dm<sup>3</sup>. The ozonation was performed for the initially acidified liquor (pH 3.5) and the TOC removal rate ranged from 7% (5 min of the process) to 13% (60 min of the process).

After 60 minutes of the process, the TOC value reduced from 550 mg/dm<sup>3</sup> to 451 mg/dm<sup>3</sup>. It was found that the landfill leachate ozonation process occurs most effectively when their pH is initially at the level of 8.5. After 60 minutes, the TOC removal rate reached 37% (346 mg/dm<sup>3</sup>). Further alkalization of raw leachate to pH=10 resulted in a slight decline in the removal rate to 25% (412 mg/dm<sup>3</sup>). Similar effects were observed when the landfill leachate reaction was neutral. The TOC removal rate reached 28% (396 mg/dm<sup>3</sup>). These changes are illustrated in Fig. 2a. At this stage, the changes in the TOC removal rate were also analysed. For a specific time range (from 5 min to 30 min), the TOC degradation process was the first order reaction which then was transformed into a quasi-static reaction (Fig. 2b). Assuming that the decomposition of organic compounds determined as TOC in the ozonation process was the first order reaction, a reaction rate constant was determined based on the Langmuir-Hinshelwood formula [Kudlek et al. 2017].

The analysis of the results obtained for constant TOC degradation rates revealed that the oxidation of organic compounds contained in landfill leachate occurs much faster in the first minutes of the process. The value of  $k_{rTOC}$  for wastewater with pH=3.5, pH=7.0, pH=8.5 and pH=10 in the 5th minute of the process was 0.014 min<sup>-1</sup>, 0.027 min<sup>-1</sup>, 0.054 min<sup>-1</sup> and 0.023 min<sup>-1</sup>. In the 60th minute of the process, the value of these coefficients were substantially reduced and amounted to 0.0039 min<sup>-1</sup> (pH=3.5), 0.0066 min<sup>-1</sup> (pH=7.0), 0.0092 min<sup>-1</sup> (pH=8.5) and 0.0057 min<sup>-1</sup> (pH=10).

The second step of this stage of the examinations was to evaluate the effect of the contaminant removal from the landfill leachate on the amount of the ozone supplied to the reaction chamber. The ozone dose was changed from 10 mg/dm<sup>3</sup> to 40 mg/dm<sup>3</sup>. The COD and TOC of the raw landfill leachate were 2885 mg/dm<sup>3</sup> and 550 mg/dm<sup>3</sup>. The worst effects of ozonation of contaminants determined as COD and TOC were observed when the lowest ozone dose was used. The 60-minute period of ozonation contributed to the removal of contaminants denoted as COD and TOC by 37% (220 mg/dm<sup>3</sup>) and 42% (1673 mg/dm<sup>3</sup>). The double ozone dose (20 mg/dm<sup>3</sup>) resulted in the increase in the removal rates for TOC (by 19%)

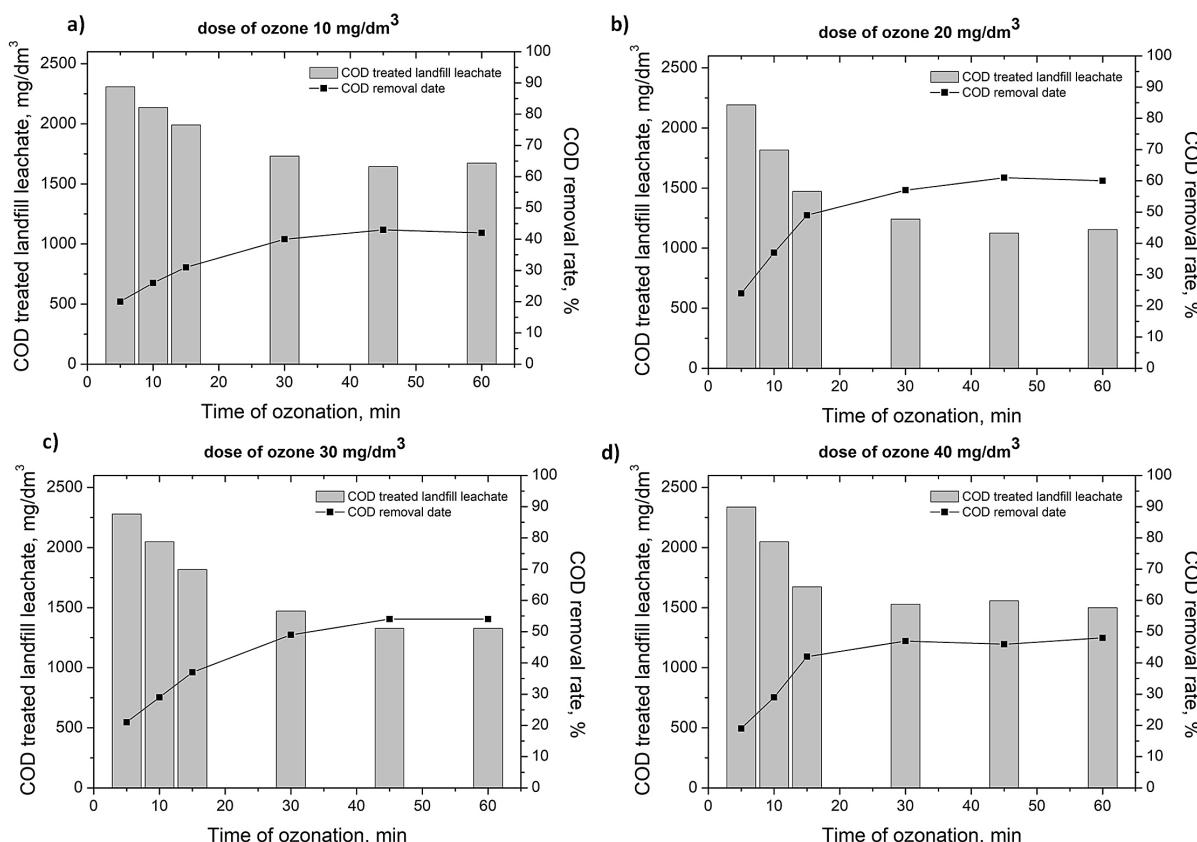


**Figure 2.** Effect of pH on the ozonation and removal of TOC- C/Co (a) and  $\ln C/C_0$  (b)

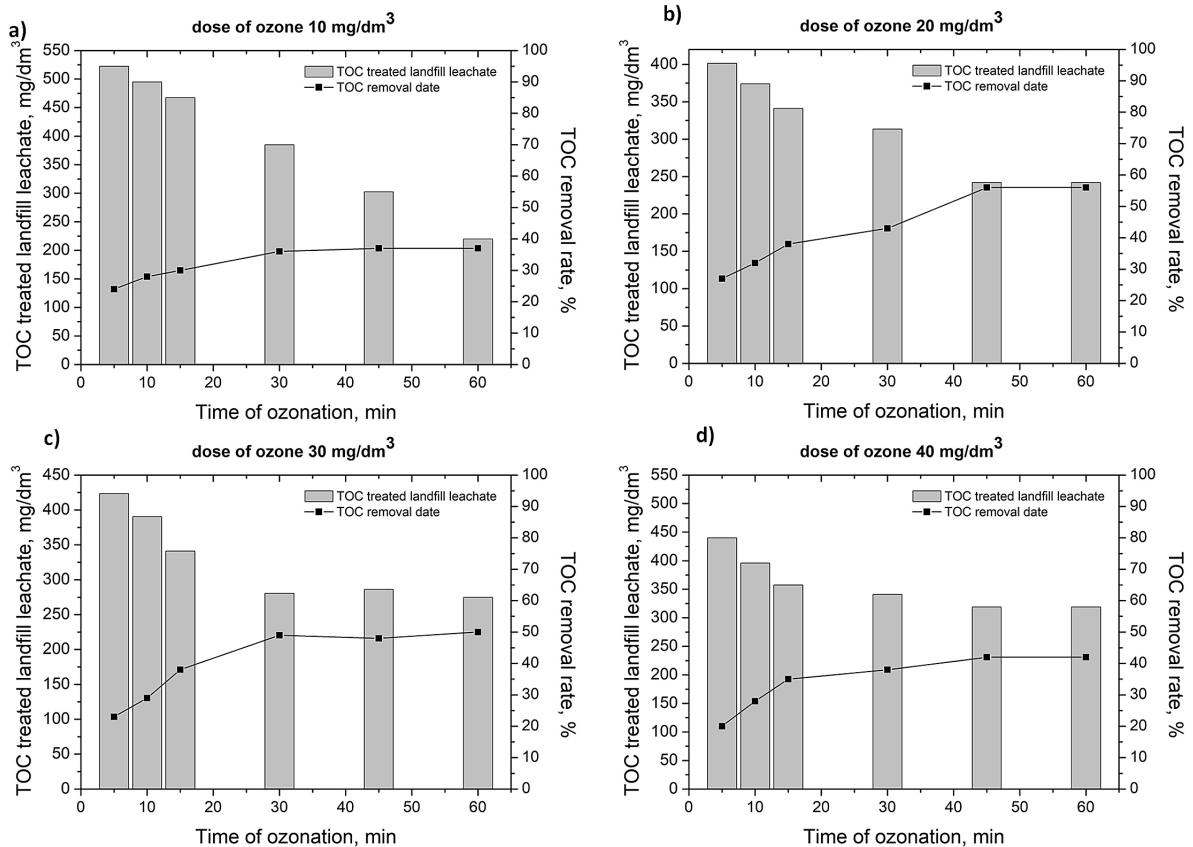
and COD (by 18%). Further increase of the ozone dose resulted in the reduction in the effectiveness of contamination oxidation. The rate of COD removal from landfill leachate after an hour process of ozonation at the ozone dose of  $30 \text{ mg/dm}^3$  was 54%, whereas the COD value for treated leachate was  $1327 \text{ mg/dm}^3$ . With this ozone dose, the rate of TOC removal was 50%, whereas its content in the treated landfill leachate reduced to the level of  $275 \text{ mg/dm}^3$ . It was found that for all the used doses of ozone, the elongation of the time of the

process to over 45 minutes did not lead to an increase in the oxidation of the contaminants contained in the landfill leachate. These changes are illustrated in Figures 3 and 4.

After determination of the most advantageous ozone dose ( $20 \text{ mg/dm}^3$ ) the BOD was evaluated during a 60 minute process of landfill leachate oxidation. After the 5th minute of the ozonation process, the value of BOD reduced from the level of  $190 \text{ mg/dm}^3$  to  $135 \text{ mg/dm}^3$ . Extension of the ozonation time to 15 minutes resulted in



**Figure 3.** The effect of the ozone dose on the COD removal rate



**Figure 4.** The effect of the ozone dose on the TOC removal rate

the increase in its removal rate by another 30%, i.e. to the level of 59% (78 mg/dm<sup>3</sup>). After 30 minutes and 60 minutes of ozonation, the value of the BOD did not change and was at a similar level of 42 mg/dm<sup>3</sup>.

Leszczyński et al. [2016] conducted research on the use of the ozonation process for stabilized landfill leachate treatment. The average values of its main parameters were: pH 8.32, COD 870 mg/dm<sup>3</sup>, BOD 90 mg/dm<sup>3</sup>, NH<sub>4</sub><sup>+</sup> 136.2 mg/dm<sup>3</sup>, UV254 absorbance 0.312 and turbidity 14 NTU. The ozone dosages were used in the range of 115.5 to 808.5 mg/dm<sup>3</sup> of the leachate. The maximum COD, colour and UV254 absorbance adjustment were 37.3%; 81.6% and 59.2%, respectively, by applying a high ozone dose of 808.5 mg/dm<sup>3</sup>. After oxidation, the ratio of BOD/COD was increased from 0.1 up to 0.23 [Leszczyński et al. 2016].

#### Treatment of landfill leachate using the system of O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub> (stages 2)

At two next stages of the examinations, the attempts were made to intensify the ozonation process by its combination with another unit pro-

cess. In the first step, the ozonation process was supported by the effect of hydrogen peroxide. Four doses were used in the experiment, with the mass ratio of H<sub>2</sub>O<sub>2</sub> to COD of raw landfill leachate of 2.5:1, 5:1, 10:1 and 20:1. The ozone dose was maintained at the level of 20 mg/dm<sup>3</sup>.

It was found that during the process that combines ozonation with hydrogen peroxide (system O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>) at the lowest dose (COD: H<sub>2</sub>O<sub>2</sub>=1:2.5), the effectiveness of oxidation of the contaminants denoted as COD and TOC was the lowest. After 5 minutes of the process, the COD removal rate was 46% and its extension to 60 minutes caused an increase in the efficiency of oxidation of contaminants to 72% (COD of the treated landfill leachate: 807 mg/dm<sup>3</sup>). With this dose of the hydrogen peroxide, the TOC removal rate following an hour of ozonation was 70% and its value in the raw landfill leachate was reduced from 550 mg/dm<sup>3</sup> to 165 mg/dm<sup>3</sup>.

The most effective process supported by H<sub>2</sub>O<sub>2</sub> occurred when the ratio of COD:H<sub>2</sub>O<sub>2</sub> was 1:10. After 45 minutes and 60 minutes of the combined process (O<sub>3</sub>+H<sub>2</sub>O<sub>2</sub>), the COD value of the treated landfill leachate was similar, with 375 mg/dm<sup>3</sup> (87%) and 403 mg/dm<sup>3</sup> (86%). The degree of

TOC removal after 60 minutes of the treatment process reached the level of 83%, and its value in the treated leachate was 93 mg/dm<sup>3</sup>.

Figure 5 illustrates the changes in TOC (a) and COD (b) of the treated landfill leachate depending on the dose of hydrogen peroxide.

The research confirms that the support of ozone treatment with H<sub>2</sub>O<sub>2</sub> results in an increase in the efficiency of stabilized leachates treatment [Amaral-Silva et al. 2016; Tizaoui et al. 2007]. In the Amaral-Silva studies, the highest organic load removal and biodegradability improvement was observed with the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process using 4 g/dm<sup>3</sup> H<sub>2</sub>O<sub>2</sub>. This system was able to eliminate 45% of the COD, 89% of the leachate BOD/COD ratio from 0.05 to 0.29 permitting the treated wastewater for the local sewage collector [Amaral-Silva et al. 2016]. Tizaoui et al. 2007 found that the ozone efficiency was almost doubled when combined with hydrogen peroxide at 2 g/dm<sup>3</sup> and higher. H<sub>2</sub>O<sub>2</sub> 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 [Tizaoui et al. 2007].

#### Treatment of landfill leachate using the system of O<sub>3</sub>+US (stage 3)

The last stage of the experiment was aimed at examining the effect of ultrasonic waves (US) on the change in the efficiency of treatment of landfill leachate subjected to ozonation. It was assumed that the free radicals of H·, HO·, HOO·, ozone, and hydrogen peroxide generated through the effect of ultrasonic waves should contribute to the increased degree of oxidation and/or destabilization of the organic substance compared to the independently performed ozonation process.

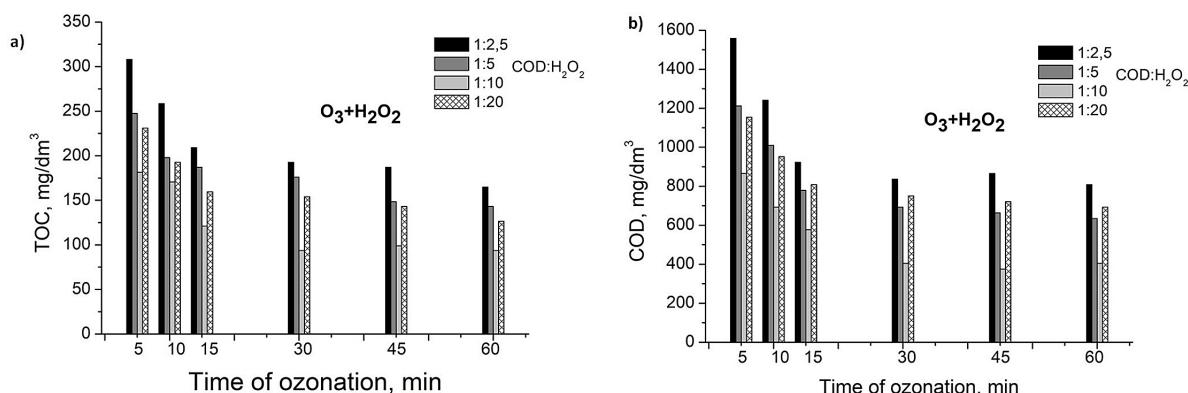
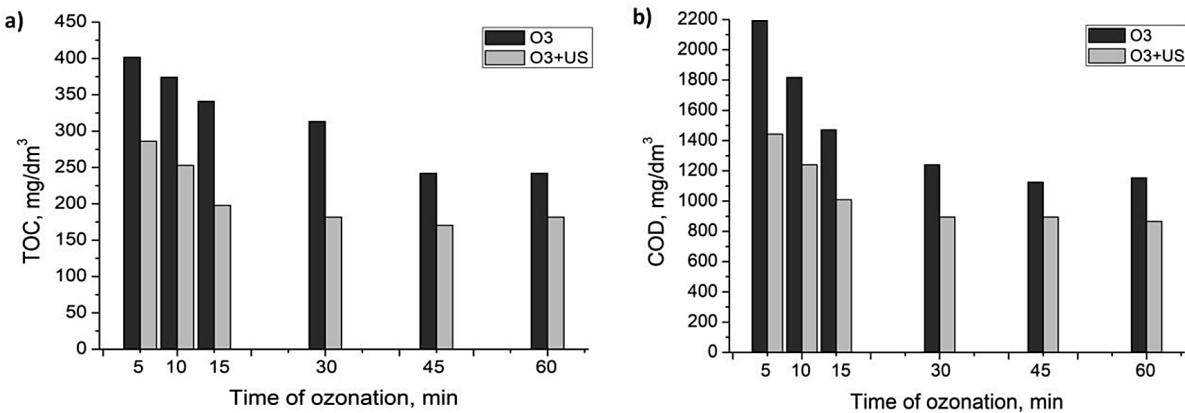


Figure 5. Changes in TOC (a) and COD (b) of the treated leachate depending on the dose of hydrogen peroxide

The examination performed by the authors previously demonstrated that the most effective sonication process occurs at the vibration amplitude of 25 µm and reaction time of 300 seconds. The process of liquor sonication substantially affected the generation and release of aliphatic compounds. Furthermore, a substantial number of compounds with the -OH functional group that can originate from alcohols and carboxyl acids was observed. [Kwarcia-Kozłowska and Sławik-Dembiczak 2016]. The value of acoustic energy supplied to the landfill leachate sample for such parameters of the ultrasonic field was on average 32459J. The changes caused in liquors are connected with e.g. cavitation. It was found that with these parameters of the ultrasonic field, the intensity of the ultrasound wave was higher than the theoretical threshold of cavitation (1.0 W/cm<sup>2</sup>) and was on average 1.34 W/cm<sup>2</sup> [Kwarcia-Kozłowska and Sławik-Dembiczak 2016].

Figure 6 compares the value of organic contaminants determined as COD and TOC in the independent process of ozonation with the process where ozonation effect was intensified by ultrasound waves.

It was found that it is more advantageous to conduct the process of landfill leachate treatment in the combined system (system O<sub>3</sub>+US), since the level of COD leachate treated after each analysed time of the process was on average by 370 mg/dm<sup>3</sup> lower, compared to the liquors which were only subjected to ozonation. After 60 minutes of ozonation and combination of ozonation with sonication, COD in the treated leachate was 1154 mg/dm<sup>3</sup> and 865 mg/dm<sup>3</sup>. In the case of TOC, the landfill leachate treated using the integrated system was characterized by lower value of the index by 126 mg/dm<sup>3</sup>, on average. Furthermore, the time of the process of leachate



**Figure 6.** Changes in TOC (a) and COD (b) of the treated leachate in  $O_3$  and  $O_3+US$  system

treatment using the  $O_3+US$  method for over 15 minutes (TOC) and 30 minutes (COD) did not impact on the improvement in oxidation of these contaminants.

The last step was the comparison of the results obtained in individual systems of landfill leachate treatment. The values in the tables represent the results obtained in each of the systems under most advantageous conditions (Table 1). It was found that the landfill leachate can be treated in the arrangement that combined ozonation with the addition of hydrogen peroxide ( $COD:H_2O_2=1:10$ ). The value of COD, TOC and BOD in such landfill leachate was lower compared to independent ozonation process by 65%, 62% and 36 %, respectively. This landfill leachate is planned to be additionally treated using the low-pressure membrane processes (e.g. ultrafiltration).

## CONCLUSIONS

The results obtained in the study led to the following conclusions:

1. The landfill leachate ozonation process occurs most effectively if the pH is 8.5. After 60 minutes of ozonation, the TOC removal rate reached 37% (346 mg/dm<sup>3</sup>);

2. It was found that the ozonation of leachate is most effective if its dose is 20 mg/dm<sup>3</sup>;
3. The most advantageous system of landfill leachate treatment was the the arrangement that combined ozone with hydrogen peroxide ( $COD:H_2O_2=1:10$ ). The value of COD, TOC and BOD in such leachate was lower compared to independent ozonation process by 65%, 62% and 36%, respectively.
4. Inclusion of the sonication process in ozonation of landfill leachate resulted in a reduction in COD and TOC by 370 mg/dm<sup>3</sup> and 126 mg/dm<sup>3</sup> compared to ozonation alone.

## Acknowledgements

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**Table 1.** Comparison of the quality of landfill leachate treated in the examined combination systems

Indicator	Raw Landfill leachate	Purification system applied (characteristics of treated landfill leachate – after 60 min)			Permissible Standards
		$O_3$	$O_3+H_2O_2$	$O_3+US$	
COD, mg/dm <sup>3</sup>	2885	1154	404	865	125
BOD, mg/dm <sup>3</sup>	190	42	27	32	25
TOC, mg/dm <sup>3</sup>	550	242	93	181	30

\* Regulation of the Ministry of Environmental Protection, Natural Resources and Forestry of 18 November 2014 on the classification of water and conditions the sewage discharged to waters and soil should satisfy.

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