



# **Investigation on Landfill Leachate Biodegradability Improvement by Use of Hydrodynamic Cavitation and Ozone**

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## **1. Introduction**

Landfilling is one of the most common and the cheapest method for disposal of municipal waste. Economically, landfill method constitutes a large waste of energy and resources. However, this loss can be diminished by applying a thermal waste utilization [5, 16]. Simultaneously, many of the oil and natural gas resources have already been completely exhausted [15, 17, 20].

From an ecological viewpoint, the main consequence of organic waste decomposition is the emission of methane. Many efforts are underway to collect the gas and use it as an energy source. Furthermore, the attempts to treat landfill sites like bioreactors producing biogas for energy purposes have been made. In order to intensify the biogas production the co-digestion with sewage sludge from wastewater treatment plant is used [13, 14].

Moreover, the generation of highly contaminated leachate is another consecutive disadvantage of waste disposal in landfills. Because of the variable leachate composition affected by waste characteristics, seasonal weather variation and the age of the landfill, effective and economically efficient leachate treatment methods are difficult to find [19]. It is reported in the literature that biological treatment of old leachates (>10 years) is limited by the presence of toxic and recalcitrant contaminants, which hinder the viability of activated sludge [4]. In this situation various advanced

oxidation processes (AOP) can be helpful by causing the abatement of refractory COD load and the enhancement of the biodegradation (raise of the BOD<sub>5</sub>/COD ratio). These processes are based on the generation of oxidizing agents, mainly hydroxyl radicals, which are extremely reactive and non-selective [6, 18]. An alternative method for leachate utilization can be the co-digestion with sewage sludge from a municipal wastewater treatment plant [10, 11]. In order to improve the biodegradability of leachate an ozone treatment can be used [9].

Ozone can transform recalcitrant organic compounds in the leachate into lower molecular weight compounds and reacts with a great number of non-biodegradable compounds [8]. In an ozonation process the oxidation can utilize two mechanisms: a direct way which involves the reaction between molecular form of ozone and the dissolved compounds or a radical way which involves the reaction between the radicals produced by ozone decomposition and the dissolved compounds [23]. The main driving mechanism in the degradation of pollutants using hydrodynamic cavitation is the generation of free radicals in extreme conditions of pressure and temperature [2, 3]. The use of cavitation enhances the rates of degradation due to the generation of additional free radicals [12] and thus, an amalgamation of the two methods is expected to give synergistic results. In the article the ozone oxidation with hydrodynamic cavitation was applied to improve leachate biodegradability.

## **2. Materials and methods**

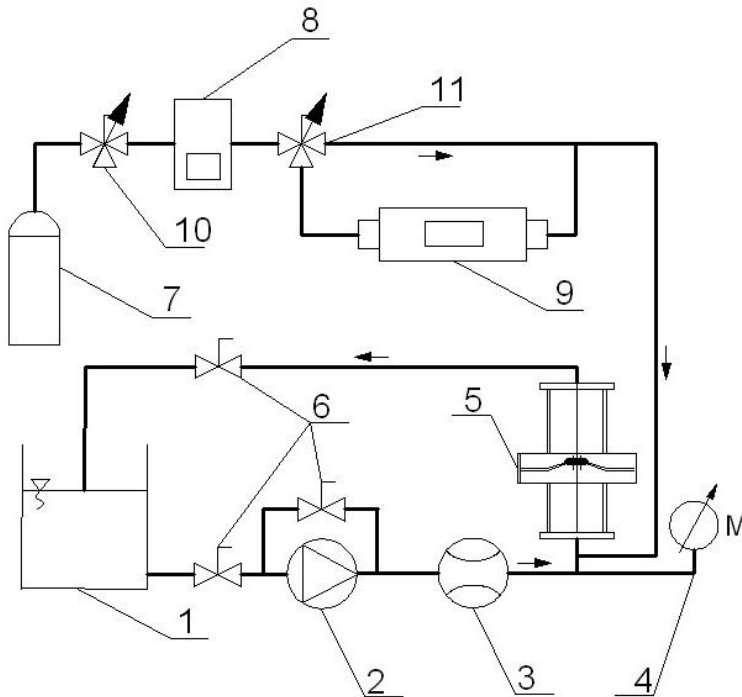
### **2.1. Materials**

The landfill leachate samples were collected from the Rokitno Landfill, which is located near Lublin city, in South-Eastern Poland. The necessary quantity of the leachate was collected to containers, transported to the laboratory and analyzed just after the arrival.

### **2.2. Experimental set-up**

The oxidation of the leachate was carried out in the experimental reactor. Figure 1 shows the schematic representation of hydrodynamic cavitation with the ozonation reactor set-up. The system used in this experiment consists of a tank with the capacity of 30 L (1) connected to the WILO pump (2), which allows to recirculate leachate within the hydro-

dynamic cavitation reactor (5). The pump flow is measured by an electromagnetic flow meter (3). Other components of the system are manometer (4) and valves (6). Ozone was generated in the BMT ozone generator (8), using medical oxygen as the feed gas (7). The concentration of ozone was monitored by the BMT ozone analyzer (9).



**Fig. 1.** Schematic diagram of ozone oxidation in conjunction with hydrodynamic cavitation system: 1 – tank, 2 – rotor pump, 3 – electromagnetic flow meter, 4 – manometer, 5 – hydrodynamic cavitation reactor, 6 – valves, 7 – oxygen, 8 – ozone generator, 9 – ozone analyzer, 10 – flow controller

**Rys. 1.** Schemat stanowiska laboratoryjnego kawitacji hydrodynamicznej w połączeniu z ozonowaniem: 1 – zbiornik, 2 – pompa wirowa, 3 – przepływomierz elektromagnetyczny, 4 – manometr, 5 – reaktor hydrokawitacyjny, 6 – zawory, 7 – tlen, 8 – generator ozonu, 9 – miernik ozonu, 10 – regulator przepływu

The hydrodynamic cavitation system operated in recirculated mode. The inductor of cavitation was a multiplate hole orifice plate. The

detailed description of the cavitation reactor used in the experiment is presented elsewhere [7].

### 2.3. Procedure

The process of hydrodynamic cavitation in conjunction with ozonation was carried out for 30 min. The flow rate of the ozonator gas stream was maintained at 0.95 L/min with the ozone concentration of 30 mg/L. The circulating flow rate was 25.2 L/min. The pressure in the system was maintained at the level of 7 bar.

Samples were taken at defined time intervals (2, 5, 10 and 30 min) and analyzed for temperature, pH, COD, BOD<sub>5</sub>, TOC, TS, VS, VFA and alkalinity. The TS, VS, BOD<sub>5</sub> and alkalinity measurements followed the Polish Standard Methods. The pH and temperature of the samples were determined using an electronic pH meter. The COD and VFA were measured with the HACH DR 3900 spectrophotometer. The analysis of total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC) was carried out by Shimadzu TOC-5050A Analyzer.

### 3. Results and discussion

Selected chemical parameters assayed in the leachate during the experiment are shown in Table 1. Before the experiment a control sample was taken to compare the results obtained from an experimental sample. The biodegradability of the leachates was evaluated through the determination of the BOD<sub>5</sub>/COD ratio. According to the literature landfills with leachates that exhibit low biodegradability (BOD<sub>5</sub>/COD ratio < 0.1) can be considered as stabilized [22]. The high COD concentration together with a low value of the BOD<sub>5</sub> concentration in leachate indicate that leachate contains macromolecular organic substances, humic and fulvic acids, which are not easily degradable [1]. In the research, leachate with COD values of about 6000 mg L<sup>-1</sup> and BOD<sub>5</sub> concentration of about 270 mg L<sup>-1</sup> (BOD<sub>5</sub>/COD ratio of 0.045) was studied. With such parameters the leachate can be classified as refractory to biological treatment. Consequently, in this case better results can be expected by applying advanced oxidation processes.

The results for BOD<sub>5</sub>, COD concentration and BOD<sub>5</sub>/COD ratio after the treatment, compared with initial concentration of control sample are shown in Figure 2. Cavitation with ozone improved leachate biodeg-

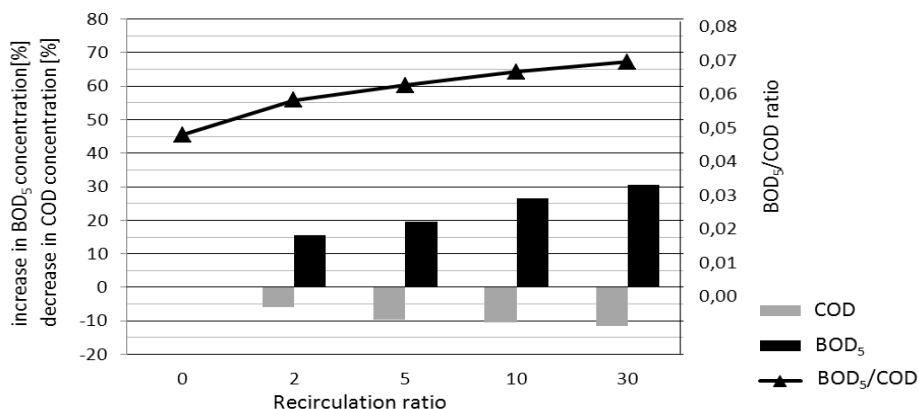
radability ( $BOD_5/COD$  ratio) from 0.045 to 0.067 after 30 recirculation cycles. In the experiment the COD concentration decreased by 11%, while the  $BOD_5$  concentration increased by 31%. Tizaoui et al. [21] observed the COD removal of about 27% for leachate from six year old landfill after 1 h treatment. In turn, Cortez [4] during the researches on leachates from old landfill achieved the improvement of the  $BOD_5/COD$  ratio from 0.01 to 0.15 after 40 min treatment using Fenton reaction together with the ozonation process.

**Table 1.** Characteristics of landfill leachate used in the experiment

**Tabela 1.** Charakterystyka odcieków ze składowiska odpadów wykorzystywanych w badaniach

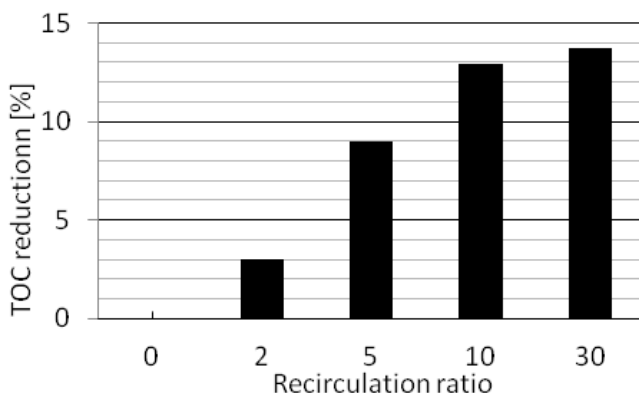
Parameters	Value
pH	8.2±0.12
COD [ $mg L^{-1}$ ]	5969±320
TOC [ppm]	1736±113
TC [ppm]	5198 ±72
IC [ppm]	3458±112
$BOD_5$ [ $mg L^{-1}$ ]	270±68
$BOD_5/COD$	0.045±0.014
TOC/COD	0.29±0.02
VFA [ $mg L^{-1}$ ]	1205±73
alkalinity [ $mg L^{-1}$ ]	15900±418
TS [ $g kg^{-1}$ ]	14.85±0.38
VS [ $g kg^{-1}$ ]	2.49±0.3

Figure 3 shows the effect of recirculation cycles of cavitation on TOC concentration. For 30 recirculation cycles, the decrease of TOC concentration was about 13.7%. Considering the results obtained, the greatest intensification process was observed during the first 10 min. Compared to the initial value, the degradation of TOC reached about 12.8% after 10 recirculation cycles. If the experiment was prolonged, even higher removal rates might be reached however the expected improvement would be rather poor considering the increase of energy costs. Instead of extending the process the change of ozone doses or the modification of the operating parameters of hydrodynamic cavitation setup could be a better solution to optimize the process.



**Fig. 2.** Effect of recirculation ratio of cavitation with ozonation on COD and BOD<sub>5</sub> concentration and BOD<sub>5</sub>/COD ratio

**Rys. 2.** Wpływ stopnia recyrkulacji w układzie kawitacji z ozonowaniem na stężenie ChZT, BZT<sub>5</sub> oraz wartość współczynnika BZT<sub>5</sub>/ChZT



**Fig. 3.** Effect of recirculation ratio of cavitation with ozonation on TOC concentration

**Rys. 3.** Wpływ stopnia recyrkulacji w układzie kawitacji z ozonowaniem na zmniejszenie zawartości OWO

## 4. Conclusions

In the article the possibility of improving the biodegradability of the leachate by hydrodynamic cavitation and ozone was investigated. The leachate used in the experiment had a very low biodegradability (BOD<sub>5</sub>/COD of 0.045) and during the experiment it was improved

(BOD<sub>5</sub>/COD of 0.067). In the study the 11% reduction of COD and 31% growth of BOD<sub>5</sub> was achieved. According to the results obtained, it can be assumed that cavitation with ozonation process can rearrange molecular structures of organic matter and transform the non-biodegradable organics to more biodegradable forms.

The future research will focus on optimising the method by changing the ozone doses and cavitation conditions in order to obtain more biodegradable leachate.

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## **Badania poprawy biodegradowalności odcieków ze składowisk odpadów z wykorzystaniem kawitacji hydrodynamicznej z ozonowaniem**

### **Streszczenie**

Odcieki ze składowisk odpadów zawierają w swoim składzie związki refrakcyjne oraz niebiodegradowalne substancje organiczne, które utrudniają lub całkowicie uniemożliwiają oczyszczanie metodami biologicznymi. Za miarę podatności odcieków na biodegradację przyjmuje się wartość współczynnika  $BZT_5/ChZT$ , która dla odcieków ze składowisk o wieku ponad 10 lat wynosi mniej niż 0.1. Metody zaawansowanego utleniania takie jak kawitacja i ozonowanie mogą wpływać na biodegradowalność odcieków poprzez zmianę struktury cząsteczkowej i rozkład związków wysokocząsteczkowych do niskocząsteczkowych. Kawitacja powoduje rozpad cząsteczek na rodniki i generowanie rodników hydroksylovych ( $\cdot OH$ ), o wysokim potencjalnie utleniającym oraz inicjowanie dalszych łańcuchowych reakcji utlenienia i degradacji. Kawitacji towarzyszą również zjawiska wtórne natury mechanicznej, chemicznej i termicznej.

W niniejszej pracy przedstawiono wyniki badań prowadzonych w zakresie podczyszczania odcieków ze składowiska odpadów za pomocą metody kawitacji hydrodynamicznej i ozonowania. Do badań wykorzystano odcieki ze składowiska odpadów komunalnych charakteryzujące się bardzo małą biodegradowalnością (wartości współczynnika  $BOD_5/COD$  0.045), o stężeniu  $ChZT$  5969 mg/L i  $BZT_5$  270 mg/L. Eksperyment przeprowadzono w czasie 30 minut, w czasie którego do układu kawitacji podawano ozon w sposób ciągły, przy zastosowaniu dawki ozonu 30 mg/L odcieków. Przeanalizowano zmiany w zakresie stężenia  $ChZT$ ,  $BZT_5$ ,  $OWO$  oraz współczynnika  $BZT_5/ChZT$  w zależności od ilości cykli recyrkulacji. Uzyskane wyniki wskazują na możliwość zastosowania przedstawionych procesów do poprawy biodegradowalności odcieków ze składowiska odpadów komunalnych.