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## Characterization of the Organic Fraction of Pretreated Leachate from Old Landfill after Sonication Exposure

### Charakterystyka frakcji organicznej odcieków ze starego składowiska po zastosowaniu sonifikacji

Collection of municipal waste in landfills, even properly designed and operated, is an important issue in environmental engineering. These are formed by the infiltration of rainfall through the waste bed and eluting with the organic and inorganic compounds, often toxic nature. So far, over 200, have been identified which are organic substances leachate contamination, as many as 35 belongs to the so-called "priority pollutants". By the decrease in the concentration of organic compounds in the leachate decrease the value of biological and chemical oxygen demand which is dictated by stabilization of landfill as lengthening the time of its life. However, the indicator  $BOD_5$  decreases faster as compared to COD therefore  $BOD_5/COD$  ratio is reduced to as low as 0.06. The leachate produced in mature landfills appears to be the presence of significant amounts of humic acid with very stable structure difficult to breach by bacteria. It was assumed that ultrasonic waves induce change in the structure of organic compounds and contribute to the acceleration of the biodegradability, among other substances in the effluents refractive thereby improve the efficiency of the biological purification processes. For sonification leachate used ultrasonic disintegrator type vibro goal Sonics (40 kHz). The range of vibration amplitude was varied in the range from 25 to 123  $\mu m$  and exposure time (sonification of leachate) from 60 to 720 seconds. Also the measuring of the size of the energy produced during sonication sonochemical leachate was made. It was found, inter alia, that the sonification process of effluents clearly influenced the formation and release of aliphatic compounds. The  $-CH_2$  and  $-CH_3$  groups can be released from the humic compounds or aromatic combinations. It was also observed the formation of substantial amounts of compounds with the functional hydroxyl group, which might be derived from alcohols and carboxylic acids. These changes suggested a breach of the chemical structure of organic compounds contained in the leachate, so that, the chemical structure of the formed compounds was more susceptible to biodegradation. The study also determined the effect of ultrasonic field on the evolution of the  $BOD_5$  treated leachates and  $BOD_5/COD$  ratio. The  $BOD_5$  sharp increase was observed at the time of sonification of leachate in the range of 60 to 300 s in the whole studied range of amplitudes. This suggests that by the action of the ultrasonic field generated in the effluents of chemical compounds had greater biodegradability. The process confirmed by the change in the ratio of  $BOD_5/COD$ . The highest value of  $BOD_5$  indicator ( $460 \text{ mg/dm}^3$ ) was at the time of subjecting the leachate impact of ultrasound using amplitude equal to the size of 25  $\mu m$  and for the time of sonification equal 300 s. In this case the  $BOD_5/COD$  factor increased to 0.12, and it was about 26% higher as compared to the value of this indicator for leachate no-sonicated (0.089).

**Keywords:** landfill leachate, IR spectra, ultrasound field, biodegradation

## Introduction

Nuisance of landfill in natural environment is associated with landfill odours, noise, rodent and insect expansion, landfill gas emission and, above all, the risk of pollution of groundwater and surface water by leachate [1-3]. The term 'leachate' means the water generated in landfills due to seepage through the bed of rainwater. They elute organic and mineral compounds resulting from biological and physico-chemical changes from the landfills waste. The source of leachate can also be surface water inflow to the storage of waste, and to a small extent, the water contained the waste and derived from the decomposition of organic substances [2, 4-7].

The amount and composition of leachate depends on many factors, which mainly include:

- the topography of the land on which the landfill was located,
- technique for landfill,
- type of waste and the degree of fragmentation,
- hydrogeological and meteorological conditions (e.g. rainfall, humidity and evaporation rate),
- the age of the landfill,
- biochemical and physical changes occurring in the waste [8-11].

Quantity of generated leachate is also limited by the age of the landfill. On young landfill leachate production is slightly smaller compared to the old (over 10 years of operation). This is due to the decreasing water retention capacity of the waste and increasing over time stabilization of organic substances [9, 12]. Due to inter alia the varied composition of the waste and the variety of storage technologies leachate show a different and difficult to predict the composition. In addition, as a result of biochemical processes in the deposited, waste is changing the nature of the leachate and their composition reflects the degree of decomposition of organic matter [8].

Residual water from young landfill (less than 5 years) contain significant amounts of readily biodegradable products of acid fermentation such as: volatile fatty acids, alcohols and ketones. They are characterized by pollutants that make reach high value of the parameters related to the organic pollution BOD<sub>5</sub> and COD which the ratio reaches high values above 0.7 which shows the ready biodegradability pH of the leachate is also slightly acidic due to the presence of significant amounts of volatile fatty acids [8-10, 12].

Over the time as a result of a reduction in the concentration of organic compounds in the leachate the value of biological and chemical oxygen demand which is dictated by the stabilization of the landfill as lengthening the time of his life decreased. However, BOD<sub>5</sub> decreases faster than COD and therefore BOD<sub>5</sub>/COD ratio is reduced to a level as low as 0.06 [13]. The leachate produced in mature landfills notes the presence of significant amounts of humic acids having a very stable structure difficult to breach by bacteria. Therefore, the purification efficiency by the biological method of activated sludge is not very high [8, 13].

With age of the storage the value of the ratio of mineral to organic compounds is reduced. In the case of young landfills takes on a value of 2 and for many years often reduced to approx. 0.1. During anaerobic fermentation organic materials are biodegradable and eluted while mineral are only leaching. The ratio of ion concentration of  $\text{SO}_4^{2-}/\text{Cl}$  is sharply decreased on the result of rapid decrease in the content of sulphates, which in anaerobic conditions are reduced to the sulphide, and then precipitated with metal ions. There is also the phenomenon of growth initially low salinity leachate “young” that as they grow older landfills typically does not exceed  $2500 \text{ mg Cl/dm}^3$ . In addition, with the passage of time increases the pH and oxidation-reduction potential of leachate [8, 9, 13]. Although many methods may apply, 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 [14].

Table 1 shows the dependence of the physicochemical properties of the leachate from the age of the landfill and the proposed methods of treatment.

Table 1. **The effect of municipal landfill age on physicochemical characteristics of leachate and efficiency of its treatment by different methods [12, 13, 15]**

Characteristics of the landfill leachate	The age of the landfill		
	< 5 years	5÷10 years	> 10 years
pH	< 6.5	6.5÷7.5	> 7.5
COD	> 10000	< 10000	< 4000
BOD <sub>5</sub> /COD	0.6÷1.0	0.1÷0.5	< 0.05
TOC/COD	< 0.3	0.3÷0.5	> 0.5
heavy metals	> 2	< 2	< 2
Treatment methods	The efficiency of the treatment process		
biological process	+++	++	+
chemical oxidation	+	++	++
chemical precipitation	+	++	+
active carbon	+	++	+++
coagulation-flocculation	++	+++	+++
reverse osmosis	++	+++	+++
ozonation	+	++	++
ion exchange	+	++	++

+ low, ++ average, +++ beneficial

Organic substances whose presence was confirmed in the leachate, ranked in order of their biodegradability. The degree of biodegradation of the compounds associated with the size of their molar mass. It has been found that the compounds having a molecular weight less than 500 Da are the substances most often readily-biodegradable. The degree of biodegradability of organic compounds decreases with the increase of the molecular weight of organic compounds [15]. Table 2

shows the size of the molar mass of organic compounds whose presence is most often found in the large quantities recorded in the leachate.

Table 2. Division of organic compounds in the leachate depending on their molar mass [15]

Type	Molecular weight organic compounds	Compounds
MW < 500 Da	Low	– volatile fatty acids – amino and organic acids – alcohols
MW 500÷10.000 Da	Medium	– carboxylic and aromatic hydroxyl groups – fulvic acids
MW > 10.000 Da	high	– humic acids – protein – carbohydrate

MW - molecular weight

There are also noted large number of bacteria that cause tuberculosis, hepatitis, and bacterial enterovirus hepatitis and meningitis. The leachate from the summer period the number of bacteria *E. coli* and *Streptococcus* may even be from  $10^{-7}$ ÷ $10^{-6}$  per 100 cm<sup>3</sup>. Special hazards are parasitological landfill leachate, that are stored in sewage sludge [3, 4, 8, 16].

Due to the fact that some organic compounds in the landfill leachate are toxically refractory and inert to biological processes (activated sludge process or methane fermentation), the process biological cannot decompose the organic pollutants in landfill leachate efficiently. Therefore it is very important to find a primary treatment process to decompose these toxically refractory and inert organic compounds firstly.

It has been many years since Richards and Loomis first used ultrasound for producing cavitation, degassing of water and for accelerating chemical reactions [17]. Ultrasound has since been used for many applications such as cell disruption, crystallization, atomization, degassing, polymerization, emulsification, nanotechnology, wastewater treatment, chemical reactions, food preservation, drug delivery, cleaning, drilling, cutting, welding, flow measurements, flow detection, ultrasonic imaging, sonar detection and many other [18].

Ultrasound is a sound, pitched above human hearing, which is used for a growing variety of purposes in diverse areas. It is considered as a “green” technology because of its high efficiency, low instrumental requirements significantly reduced process time compared with other conventional techniques and its economically viable performance.

Depending on the frequency, ultrasound is divided into three categories, namely power ultrasound (20÷100 kHz), high frequency ultrasound (100 kHz÷1 MHz), and diagnostic ultrasound (1÷500 MHz). Ultrasound ranging from 20 to 100 kHz is used in chemically important systems, in which chemical and physical changes

are desired as it has the ability to cause cavitation's of bubbles [19]. The chemical effects of ultrasound are depended on the phenomenon of acoustic cavitation. Sound is transmitted through any fluid as a wave consisting of alternating compressing and rarefaction cycles. If the rarefaction wave is sufficiently powerful, it can produce a negative pressure, which is large enough to overcome the intermolecular forces binding the fluid. As a result, the molecules are torn apart from each other and form tiny micro bubbles. These micro bubbles gradually grow during the compression-rarefaction cycles until they reach a critical size. Subsequent compression then causes the micro bubbles to collapse almost instantaneously, thereby releasing a large amount of energy. Temperatures of the order of 5000 K have been experimentally obtained and pressures of the order of 1000 atmospheres have been calculated [20].

Ultrasound treatment is one of several technologies that promote hydrolysis, the rate-limiting stage during wastewater treatment. The basic principal of ultrasound is based on the destruction of bacterial cells and difficult-to-degrade organics. In wastewater, various substances and agents collect in the form of aggregates and flakes, including bacteria, viruses, cellulose and starch. The energy produced during ultrasound treatment causes these aggregates to be mechanically broken down, altering the constituent structure of the wastewater and allowing the water to be separated more easily, because ultrasound attacks the bacterial cell walls, the bacterial cells release iso-enzymes that biocatalyst hydrolytic reactions [20]. This results in acceleration in the breakdown of organic material into smaller readily biodegradable fractions. The subsequent increase in biodegradable material improves bacterial kinetics resulting in lower wastewater quantities and, in the case of anaerobic digestion, increased biogas production. Therefore, its use is most suited to streams containing large quantities of refractory material and/or cellular matter. Wastewater are conditioned with polymers to enhance the efficiency of dewatering with presses and centrifuges but the relationship between fluid dynamics and the polymer/wastewater interaction has been shown to be critical in mixing and conditioning performance [20].

Processing and disposal of wastewater is one of the most complex environmental problems faced by the engineers as well as scientists in this field. Wastewater is composed largely of the substances responsible for the offensive, pathogenic and toxic materials. The ultrasound process does not require addition of oxidants or catalyst, and does not generate additional waste streams as compared to adsorption or ozonation processes [21].

## **1. Material and methods**

### **1.1. Landfill leachate**

Leachate was derived from regional municipal waste landfill in Sobuczyna near Częstochowa. Research has shown that analyses leachate collected during the winter

and spring were characterized by a significantly lower pollutant load (average COD were 3400 mg O<sub>2</sub>/dm<sup>3</sup>) compared with the summer and autumn (average COD were 4500 mg O<sub>2</sub>/dm<sup>3</sup>). The ratio of BOD<sub>5</sub>/COD was for the range of 0.087÷0.089 which indicated their low biodegradability (Table 3).

Table 3. Characteristics of landfill leachate from Sobuczyna

Parameter	Value	Permissible Standards*
pH	8.2÷8.6	6.5÷9.0
COD, mg/dm <sup>3</sup>	3400÷4500	125
BOD, mg/dm <sup>3</sup>	370÷420	25
Ammonia nitrogen, mg/dm <sup>3</sup>	690÷1020	10
Nitrogen, mg/dm <sup>3</sup>	730÷990	30
Phosphorus, mg/dm <sup>3</sup>	1.0	3.0
Chloride, mg/dm <sup>3</sup>	1700÷2600	1000
Sulfates, mg/dm <sup>3</sup>	450÷525	500
Suspended solids, mg/dm <sup>3</sup>	70÷100	35
Nickel, mg/dm <sup>3</sup>	0.26	0.5
Zinc, mg/dm <sup>3</sup>	1.7	2.0
Copper, mg/dm <sup>3</sup>	0.34	0.5
Cadmium, mg/dm <sup>3</sup>	0.00353	0.4
Lead, mg/dm <sup>3</sup>	0.01296	0.5
Iron, mg/dm <sup>3</sup>	3.0	10.0
Sodium, mg/dm <sup>3</sup>	1100	800
Potassium, mg/dm <sup>3</sup>	1096	80

\* Regulation of the Ministry of Environmental Protection, Natural Resources and Forestry, dated 18 November 2014, on the classification of water and conditions the sewage discharged to waters and soil should satisfy, J. Law No. 0, item 1800

## 1.2. Ultrasonic disintegrator

For sonification of leachate of ultrasonic disintegrator Sonics vibro cell was used. Ultrasonic energy (US) generated in the ceramic transducer “sandwich” was introduced into the assay medium (raw leachate) through the hub (sonotrode). The volume of each attempts landfill leachate was 500 cm<sup>3</sup>. The disintegrator Sonic vibro cell (40 kHz) stabilized amplitude was varied in increments of 25 µm to 123 µm and also be used for measuring the amount of energy produced during sonication sonochemical leaching. During the tests the monitored energy brought to the sample. As a result, it was possible to determine the size of the intensity of the ultrasonic wave (I) [22].

### 1.3. Analytical methods

Landfill leachate was sampled periodically for pH value, alkalinity, COD, BOD, ammonia nitrogen, volatile fatty acids (VFA) and chloride analyses. Chemical oxidation demand (COD) was analyzed using colorimetric tests on HACH-DR 4000 photometer. Biochemical oxidation demand - in five days (BOD) was measured with an OxiTop respirometer. The alkalinity and chloride were measured according to Standard Method [23]. The pH value was determined with a pH-meter Cole Parmer. Ammonia nitrogen and VFA were determined with the distillation method on Büchi 323-Distillation Unit. Wastewater samples were analyzed for heavy metals through inductively coupled plasma mass spectrometry (ICP-MS) analyzer.

A useful method that is often used to track changes occurring in the environment is the analysis of the infrared spectra performed by IR spectroscopy. Therefore this method was used to determine the effect of ultrasound on the structure of chemical compounds in the leachate. As a result of the IR spectrum in this area are very complex and extremely rare that two different chemical compounds were in the range of identical spectra, which practically allows an unambiguous identification. The use of a database of frequencies of existing data ranges defined chemical compounds allows for the identification of compounds in a given sample. Analysis of the infrared spectra was taken with the camera to the adsorption in the IR BIO-RAD type FTS 135 Fourier transform.

Due to the fact that wastewater include organic compounds in suspended, colloidal and dissolved form, additional studies were carried out, consisting in determining the percentages of each fraction. It is known that the greatest biological biodegradable organic compounds are those which are present in the wastewater in dissolved form. For this purpose treated leachate was filtered sequentially through a filter disk (removed organic compounds present in suspended form) and a membrane filter with a pore size of 0.45  $\mu\text{m}$  (removed dissolved organic material). Organic compounds in the form of colloidal calculated based on the difference in concentrations of organic substances in the filtrate after filtration of the sample through a filter membrane and the filter disk.

## 2. Results and discussion

### 2.1. The UD field influence on changing the form of the presence of organic compounds in the tested leachate

Sonication process is often described by the size of which is the intensity of the ultrasound wave. It is a reliable parameter specifies the amount of energy carried by the acoustic wave and reaching the surface of the center perpendicular to the direction of propagation. It is understood that in order to induce cavitation in the liquid medium of the ultrasonic wave intensity needs to be at least  $1.0 \text{ W/cm}^2$ . It was found that the intensity of the ultrasonic wave was lower than the theoretical threshold when the wastewater sonication amplitude was 25  $\mu\text{m}$  and exposure times of 120 s ( $0.91 \text{ W/cm}^2$ ) and 180 s ( $0.98 \text{ W/cm}^2$ ). The highest amount of inten-

sity of ultrasonic waves ( $5.18 \text{ W/cm}^2$ ) was observed during 600 seconds sonication with an amplitude of  $123 \mu\text{m}$  (Fig. 1).

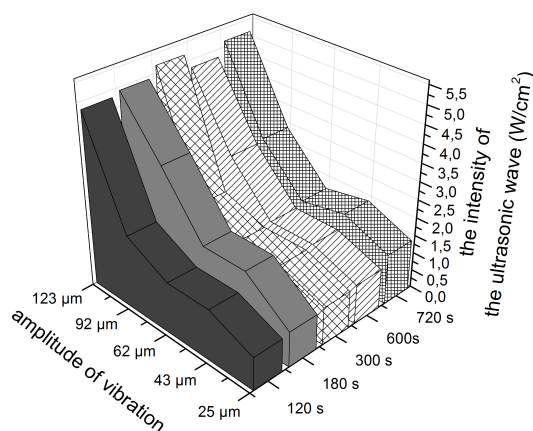


Fig. 1. The intensity of the ultrasonic wave as a function of the surface reaction vessel and the size of its amplitude

The study also determined the effect of ultrasonic field on the evolution of the BOD of treated leachates and BOD/COD ratio. The BOD and COD values characterizing the leachate that was not sonicated were respectively  $370$  and  $4150 \text{ mg O}_2/\text{dm}^3$  and their ratio stood at  $0.089$ . The BOD sharp increase was observed at the time of sonication of leachate in the range of  $60$  to  $300$  s in the whole studied range of amplitudes. This suggests that by the action of the ultrasonic field generated in the effluents of chemical compounds had greater biodegradability. The process confirmed by the change in the ratio of BOD/COD. The highest value of BOD indicator ( $460 \text{ mg O}_2/\text{dm}^3$ ) was at the time of subjecting the leachate impact of ultrasound using amplitude equal to the size of  $25 \mu\text{m}$  and for the time of sonication equal  $300$  s (Fig. 2a). In this case the BOD/COD factor increased to  $0.12$  and it was about  $26\%$  higher as compared to the value of this indicator for leachate non-sonicated (Fig. 2b).

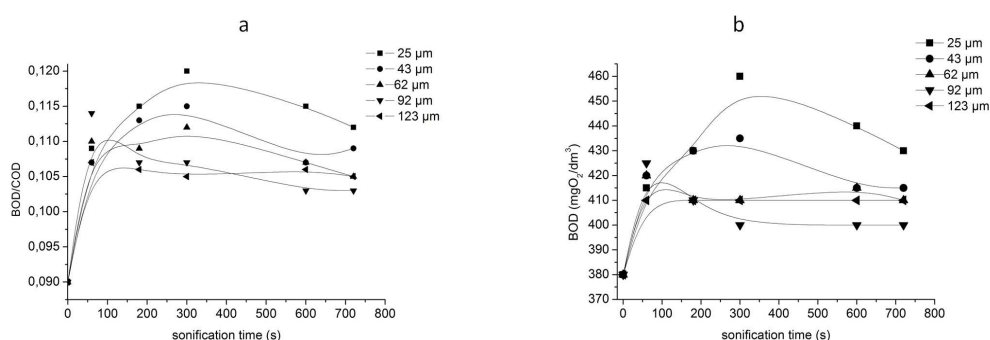


Fig. 2. Effect of sonication and size of the vibration amplitude on the size of BOD<sub>5</sub> (a) and BOD<sub>5</sub>/COD indicators (b)



Due to the fact that there were organic compounds in the landfill leachate (the amount determines the value of the COD) in the form of suspended, colloidal and dissolved, additional studies were carried out, consisting in determining the percentages of the individual fractions. It is known that the greatest biological biodegradable organic compounds were those which were presented in the wastewater in dissolved form. They were transported directly into the cells of microorganisms and transformed in the products by metabolism. Therefore, an attempt to determine changes in the percentage of individual forms in which organic compounds were present in the leachate no-sonicated and affected by ultrasonic field. Therefore, an attempt to determine changes in the percentage of individual forms in which organic compounds are present in the untreated leachate and affected by ultrasonic field using a set of the best vibration amplitude 25  $\mu\text{m}$  and variable exposure time (30÷720 s). Analysis of the results showed that increasing the time of conditioning leachate resulted in the passage of organic compounds present in the form of suspended and dissolved colloidal form. In the case of raw leachate dissolved fraction represented 77.1% of the total COD load. The fraction of suspended and colloidal amounted to 12.4 and 10.5%. At the time of sonication equal 300 s dissolved organic compounds accounted for 89.1%, while the suspended and colloidal fraction was 5.5 and 5.4% (Fig. 3). Further extension of exposure did not affect already on the percentage change in the soluble fraction of the organic matter present in the leachate.

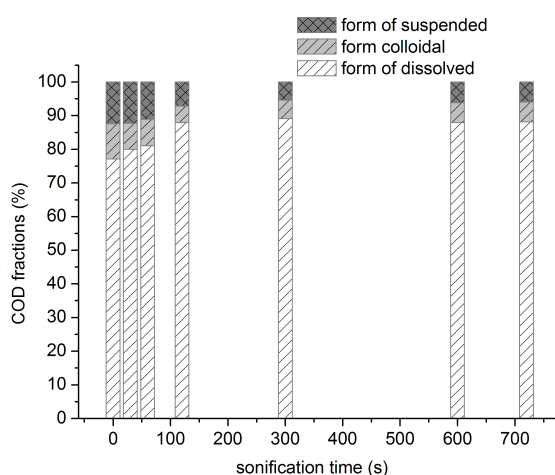


Fig. 3. Effect of sonication and size of the vibration amplitude of the size of BOD/COD indicator

## 2.2. IR technique to identify functional groups of organic compounds contained in landfill leachate

The studies were carried out using the IR technique to identify functional groups of organic compounds contained in effluents before and after treatment. Infrared analysis was performed with extracts from the leaching solvent by means of three

differing stronger absorption ranges own (not transparent to infrared radiation - Table 4).

Table 4. **The range of own absorption of solvents used in extraction process**

The solvent	Absorption frequencies, $\text{cm}^{-1}$
Carbon disulfide	2220÷2120 1630÷1428
Trichloromethane (chloroform)	3000÷2700, 820÷725
2,2,4 trimethylpentane	3000÷2500, a plurality of bands below 1500

In order to compensate the absorption of the solvent its spectrum is recorded and then it is subtracted from the sample spectrum. In certain areas of the IR spectra the solvent can be practically impermeable to infrared radiation, which prevents the formation of these areas of the spectrum of the test substance. In this case, the spectrum can be recorded under the same conditions in various solvents on the permeability of the complementary areas (transparency).

The analysis was conducted on the raw leachate and effluent conditioned in the UD (amplitude range from 25 to 123  $\mu\text{m}$  for exposure times of 60 to 720 s).

### **Carbon disulfide**

Carbon disulfide as the solvent does not have absorption bands in the range  $4000\div2500\text{ cm}^{-1}$ , which allows the identification of a stretching single bond vibration mainly O–H, N–H present in the majority of organic compounds.

Table 5. **Occurrence of compounds or functional group observed in the IR spectra of leachate dissolved in carbon disulphide**

Type of vibration	Compound or group	Absorption frequencies $\text{cm}^{-1}$	Occurrence
C–H stretching in alkanes	–CH <sub>3</sub>	2975÷2950 2885÷2860	25 $\mu\text{m}$ , 300 s 123 $\mu\text{m}$ , 180 s
	–CH <sub>2</sub>	2930÷2915 2860÷2840	
O–H stretching	$\beta$ -diketones -enol form	3000÷2700	25 $\mu\text{m}$ , 300 s 123 $\mu\text{m}$ , 180 s
stretching C–H in aldehydes	O    –C–H	2900÷2800 2775÷2650	25 $\mu\text{m}$ , 300 s 123 $\mu\text{m}$ , 180 s

The analyzes showed no absorption bands extracts samples of leachate from untreated landfills. It has been found that the size of the vibration amplitude and the duration of sonication affect changes in the IR spectra obtained predominantly in the range  $3000\div2700\text{cm}^{-1}$ . This is the range characteristic for the vibration

stretching  $-\text{CH}_2$  and  $-\text{CH}_3$  groups. A very intense band in this field appear in the leachate samples treated at amplitude size of 25  $\mu\text{m}$  and sonication time of 300 s (transmittance approx. 45%). It also occurred in the samples of effluents treated at amplitude size of 123  $\mu\text{m}$  for the sonication time of 180 s. For the other samples there was no bands observed in this range. Broad band of  $-\text{OH}$  bond of the enol form present in the range of  $3000\div 2700\text{ cm}^{-1}$  were observed only for two samples: 20  $\mu\text{m}$  at the time of 300 seconds and 123  $\mu\text{m}$  at the time of 180 seconds (Table 5).

#### **Chloroform/Trichloromethane**

IR spectra of effluents in chloroform showed bands richness mainly in two ranges of wavelength  $3750\div 3550\text{ cm}^{-1}$  and  $1160\div 960\text{ cm}^{-1}$ . The most intense was recorded in the sample of leachate treated at an amplitude of 62  $\mu\text{m}$  and sonication time 300 s. Unequivocal change in the structure of chemical compounds present in the leachate under the influence of their conditioning was evident in the wavelength range  $1160\div 960\text{ cm}^{-1}$ . The spectrum illustrating the untreated effluent in this range of wavelength was a single peak at  $1090\text{ cm}^{-1}$ . However, in samples of 25  $\mu\text{m}$  and time 180 s, 62  $\mu\text{m}$  at the time of 300 s and 123  $\mu\text{m}$  at the time of 180 s the broad bands with two asymmetric peaks were observed.

For the other samples, the absorption of infrared radiation has not been recorded. Confirmation of these changes was the transmittance in the range of  $3750\div 3550\text{ cm}^{-1}$ . The changes, however, were not intense and unambiguous. Infrared absorption spectrum of  $3750\div 3550\text{ cm}^{-1}$  is attributed to bonding  $-\text{OH}$  in water or steam. Most of the samples tested in this area showed a transmittance of 90%. Only treated leachate sample when the amplitude size of 62  $\mu\text{m}$  and exposure time of 300 seconds in this area was intense band at 70% transmittance. In this sample higher amount of hydrophilic compound than the other was registered. In the untreated effluents sample and also treated leachate were no bands at amplitude of 123  $\mu\text{m}$  and time 180 s.

The fact that sonification alters the structure of the compounds in the leachate also provides transmittance in the range of  $1160\div 960\text{ cm}^{-1}$ . The treated leachate has recorded one band at a length of  $1070\text{ cm}^{-1}$ . Treated leachate samples respectively at the amplitude of vibration and the size of the exposure time, respectively, for 180 s 123  $\mu\text{m}$ , 25  $\mu\text{m}$ , 62  $\mu\text{m}$  and 300 s and 180 s for broad band was in the form of two distinct peaks of approximately  $1070\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$ .

The effluents in the treated sample the sharp band in the range  $1600\div 1200\text{ cm}^{-1}$  was recorded, whereas in treated samples was a lack of this band.

Tables 6 and 7 show the presence of the IR spectra of the compounds included in the leachate studied dissolved in chloroform. The size of the vibration amplitude and time of sonication mainly affects change in the range of  $3750\div 3550\text{ cm}^{-1}$ . More intensive changes in the intensity of the transmittance of leachate spectra were recorded in the treated samples at the time of 180 s to 300 s.

To sum up, the process effluents sonification clearly affected the formation of the release of aliphatic compounds, hence the formation of bands in this area.

Groups  $-\text{CH}_2$  and  $-\text{CH}_3$  can be released from humus compounds or combinations of aromatic formation. It was also observed a significant number of compounds with the functional group  $-\text{OH}$ , which may be derived from alcohols and carboxylic acids. As it was mentioned earlier, these changes suggest a possible violation of the chemical structure of organic compounds in the leachate thereby give compounds of the chemical structure more susceptible to biodegradation.

Table 6. The occurrence of compounds or functional group observed in the IR spectra of leachate dissolved in chloroform in the range of  $3750\div 3550\text{ cm}^{-1}$  and  $1160\div 960\text{ cm}^{-1}$

Type of vibration	Compound or group	Absorption frequencies $\text{cm}^{-1}$	Occurrence
OH	$\text{H}_2\text{O}$	$3700\div 3530$	
C–O	$\text{R}_2\text{CH–OH}$	$1125\div 1090$	
C–O	$\text{RCH}_2\text{ OH}$	$1075\div 1000$	
C–O–C	ethers $\text{CH}_2\text{–O–CH}_2$	$1150\div 1060$	in the raw landfill leachate (without sonication)
C–N	in amines	$1090\div 1068$	

Table 7. The occurrence of compounds or functional group observed in the IR spectra of leachate dissolved in chloroform in the range of  $1300\div 2850\text{ cm}^{-1}$  and  $1600\div 1200\text{ cm}^{-1}$

Type of vibration	Compound or group	Absorption frequencies $\text{cm}^{-1}$	Occurrence
C–H in alkanes	$\text{R–CH}_3$ $\text{C–(CH}_3)_2$ $\text{C–(CH}_3)_3$	$2972\div 2952$	
O–H carboxylic acids	$\text{C–C–COOH}$ $\text{C=COOH}$	$3100\div 2900$	
C–H in aldehydes	$\text{R–CHO}$ $\text{CH=CH–CHO}$ $\text{HO–C=C–COH}$	$2900\div 2800$	
stretching C=C	in alkenes	$1650\div 1580$	in the raw landfill leachate (without sonication)
$\text{CH}_3$	$\text{N–CH}_3$ in amines	$1470\div 1430$	
$\text{CH}_3$	$\text{O}$ $\parallel$ $\text{–O–C–CH}_3$ in esters and lactone	$1450\div 1400$ $1400\div 1340$	
OH	alcohols and phenols	$1450\div 1200$	

The change in transmittance in the individual absorption bands indicate the changes occurring in the leachate under the influence of sonification. The leachate before and after sonication enter a number of different chemicals due to the nature and type of the newly created constituent groups and bonds.

The microorganisms are capable of assimilating the substance only those compounds which are hydrolyzed. The increase in transmittance in the creation of bonds OH suggests hydrophilic compounds, which strongly affects the leachate increased susceptibility to biodegradation.

## Conclusion

1. The process of sonification of leachate clearly influenced the formation and release of aliphatic compounds, hence the formation of bands in this area. Groups  $-\text{CH}_2$  and  $-\text{CH}_3$  can be released from humus compounds or combinations of aromatic formation. Furthermore, a significant number of compounds with the functional group  $-\text{OH}$ , which may be derived from alcohols and carboxylic acids was also observed.
2. The highest value of BOD ( $460 \text{ mg O}_2/\text{dm}^3$ ) adopted at the time of subjecting the leachate impact of ultrasound using the size of amplitude equal to  $25 \mu\text{m}$  and the sonication time 300 s. Ratio BOD/COD in this case increased to 0.12 and it was about 26% higher compared to the value of this ratio for untreated leachate.
3. Analysis of the results showed that the ultrasonic field leachate conditioning resulted changing of organic compounds present in the form of suspended and colloidal to dissolved form. The dissolved fraction in the raw leachate and treated leachate was 77.1 and 89.1%, respectively.

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## **Streszczenie**

**Gromadzenie odpadów komunalnych na składowiskach, nawet prawidłowo zaprojektowanych i eksploatowanych, jest istotnym zagadnieniem w inżynierii środowiska z uwagi na problemy ochrony wód gruntowych przed zanieczyszczeniem odciekami. Ocieki powstają w wyniku infiltracji opadów atmosferycznych przez złoża odpadów i wymywanie z niego związków organicznych i nieorganicznych, niejednokrotnie o charakterze toksycznym. Dotychczas zidentyfikowano ponad 200 substancji organicznych będących zanieczyszczeniami odcieków, z których aż 35 należy do tzw. „priority pollutants”. W miarę upływu czasu skutek obniżania się stężenia związków organicznych w odciekach zmniejszają się wartości**

biologicznego i chemicznego zapotrzebowania tlenu, co związane jest ze stabilizacją składowiska w miarę wydłużania czasu jego eksploatacji. Wskaźnik  $BZT_5$  szybciej maleje w porównaniu z ChZT, w związku z czym stosunek  $BZT_5/ChZT$  ulega zmniejszeniu nawet do poziomu 0,06. W odciekach powstających na „starych” składowiskach odnotowuje się obecność znacznych ilości kwasów humusowych charakteryzujących się bardzo stabilną strukturą trudną do naruszenia przez bakterie. Dlatego też efektywność ich oczyszczania metodą biologiczną osadu czynnego lub fermentacji metanowej nie jest zbyt wysoka. Założono, że fale ultradźwiękowe wywołają zmianę struktury związków organicznych i przyczynią się do przyspieszenia biodegradowalności, między innymi substancji refrakcyjnych w odciekach, dzięki czemu wzrośnie efektywność ich oczyszczania w procesach biologicznych. Do nadźwiękowania odcieków użyto dezintegratora ultradźwiękowego typu Sonisc vibro cel (40 kHz). Zakres wartości amplitud drgań zmienił się od 25 do 123  $\mu\text{m}$ , a czas ekspozycji (nadźwiękowania odcieków) od 60 do 720 s. Podczas sonifikacji dokonywano również pomiaru wielkości energii sonochemicznej wytwarzanej podczas nadźwiękowania odcieków. Stwierdzono m.in., że proces sonifikacji odcieków wyraźnie wpłynął na powstawanie i uwolnienie związków alifatycznych. Grupy  $-CH_2$  i  $-CH_3$  mogły być uwalniane ze związków humusowych lub połączeń aromatycznych; zaobserwowano również powstawanie znacznych ilości związków z grupą funkcyjną  $-OH$ , które mogły być pochodnymi alkoholi i kwasów karboksylowych. Zmiany te wskazują na naruszenia struktury chemicznej związków organicznych zawartych w odciekach, wskutek czego powstawały związki o strukturze chemicznej bardziej podatnej na proces biodegradacji. W badaniach określono także wpływ pola ultradźwiękowego na zmiany wskaźnika  $BZT_5$  oczyszczanych odcieków oraz na stosunek  $BZT_5/ChZT$ . Wyraźny wzrost  $BZT_5$  obserwowano w momencie nadźwiękowania odcieków w zakresie od 60 do 300 s w całym przebadanym zakresie amplitud. Sugeruje to, że wskutek oddziaływania pola ultradźwiękowego na odcieki powstają w nich związki chemiczne o większym stopniu biodegradowalności. Zachodzący proces potwierdziła zmiana wartości stosunku  $BZT_5/ChZT$ . Najwyższą wartość 460  $\text{mg}/\text{dm}^3$  wskaźnik  $BZT_5$  przyjął w momencie poddawania odcieków oddziaływaniu ultradźwięków przy zastosowaniu wielkości amplitudy równej 25  $\mu\text{m}$  i dla czasu nadźwiękowania 300 s. Współczynnik  $BZT_5/ChZT$  w tym przypadku wzrósł do poziomu 0,12 i był on o 26% wyższy w porównaniu do wartości tego wskaźnika dla odcieków nienadźwiękowanych (0,089).

**Słowa kluczowe:** odcieki składowiskowe, spektroskopia IR, pole ultradźwiękowe, biodegradacja