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The application of ultrasounds in oily wastewater pre-treatment

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Abstract: The aim of the study was to determine the impact of various methods of oil mixing with wastewater on properties of synthetic municipal wastewater containing edible oil (SMW+0.02% m/v rapesed oil). The study was carried out in 3L glass, cylindrical reactors to which SMW+0.02% were introduced. Various methods of its mixing with water were applied: mechanical mixing (SMW+0.02%+mixing) and sonication (SMW+0.02%+ultrasounds). The wastewater was sonicated at 35 kHz for 30 min. The constant temperature conditions were maintained during the experiment for each mixing method (15°C, 20°C and 30°C). The analysis of parameters (pH, COD, BOD₅ and long chain free fatty acids concentration) of raw wastewater and after 2, 4, 6, 24, 48 and 72 hours of inoculation was performed to determine the effect of mixing method.

The most significant changes in wastewater chemical parameters after the introduction of the oil were observed in the case of COD. For SMW+0.02%+ mixing a slow increase in COD within 24 hours of the process was observed. In the case of SMW+0.02%+ultrasounds the increase and the decrease of COD value were observed in reference to the initial value. The changes in acids concentrations observed in reactors with SMW+0.02%+ultrasounds were referred to the ones observed in reactors with SMW+0.02%+mixing but changes were more intense in the first reactor. The use of ultrasounds in pre-treatment of wastewater resulted in the intense appearance of palmitic acid for 6 hours. Regardless of the emulsion formation method (mixing or ultrasounds), the concentration of oleic acid and linoleic acid was reduced. The biggest changes in free fatty acids concentration were observed for palmitic, oleic and linoleic acids after 24 hours.

Introduction

The quality of wastewater is very important considering its further treatment in wastewater treatment plant, especially when biological methods are applied. Also, this may relate to the municipal wastewater regarded as readily biodegradable wastewater because of the fats present in wastewater in the form of an emulsion or a thin, lipid layer floating on the surface of the wastewater. The main disadvantages in that case are sudden and uncontrolled wastewater dumps as well as bringing the sewage about in tanks. The appearance of oil pollution in municipal wastewater may have a negative effect on the mechanical and biological wastewater treatment plant.

Oily wastewater is usually treated with the use of physical, chemical or biological methods. However, if a method is used only as a single stage process, it is not sufficient enough to effectively remove all contaminants, especially in the case of industrial wastewater. Nowadays, large amounts of organic pollution present in the environment, are the result of anthropogenic impacts on the environment. Hence, there exists an actual need for the use of hybrid or integrated treatment systems to remove the organic compounds. An example of such a solution is a combination of physical and chemical processes, namely membrane photocatalytic reactor (Jamly et al. 2015), dissolved air flotation and sludge dewatering (Bogacki et al. 2017). Examples of physical/chemical and biological methods are: an air flotation system and activated sludge reactor, electrocoagulation and electroflotation with membrane bioreactor, extraction and electrocoagulation with anaerobic digestion (Khoufi et al. 2008), digestion with using premixing Bacillus at 9 wt% with ultrasonic treatment and citric acid addition (Jamly et al. 2015), ultrasounds and enzymatic oil recovery (Jiang et al. 2014).

In the paper the preliminary treatment of oily wastewater with ultrasounds applied before the biological treatment, arranged in the integrated system, is proposed. Due to the literature data, the sonication process should be carried out within the low frequency ultrasounds in the range of 20 to 100 kHz and high power or high frequency in the rage of 2 to 10 MHz and low power (Fernandez-Cegri et al. 2012, Rokhina et al. 2009). A frequency power and intensity amount of energy supplied over time are two main parameters that influence the efficiency of the treatment (Tytła and Zielewicz 2016). Ultrasounds are already used at wastewater treatment plants but mostly for the processing of excess sludge i.e. for its disintegration before anaerobic digestion process. The reason behind the use of ultrasounds is the phenomenon of formation of free radicals (Nasseri et al. 2006). In wastewater



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treatment, the sonication process allows for the destruction of non-biodegradable (Yang et al. 2016), hardly biodegradable (Ramteke et al. 2015) and toxic organic compounds (Bonyadi et al. 2012, Wang & Liu 2014, Kwarciak-Kozłowska et al. 2015, Yang et al. 2016), formation of soluble organic compounds (Nasseri et al. 2006), destruction of pathogen cells (Antoniadis et al. 2007).

The maximum decomposition of cyanide (high toxicity) was performed at frequency of 130 kHz for 90 minutes i.e. 74%, but the efficiency of treatment at 35 kHz and lasting 90 minutes was only slightly lower and amounted to about 71% (Bonyadi et al. 2012). The use of ultrasounds as a single stage process is not economically justified. The combination of ultrasounds and Fenton's reagent has been used to effectively degrade refractory compounds (Wang & Liu 2014), i.e. the degradation (100% alachlor) and mineralization (46,8% TOC) of alachlor (herbicide) was obtained with using the frequency of 20 kHz (Wang & Liu 2014), the pre-treatment (22 kHz) was applied to improve biological treatment of wastewater containing benzene, toluene, naphthalene and o-xylene (Ramteke et al. 2015) and the ammunition wastewater was treated at the frequency of 20 kHz (Li et al. 2013). Ultrasounds as pre-treatment and SBR were used to increase the quality of treated wastewater from fibreboard industry (Grosser et al 2009). In the case of pharmaceutical wastewater the optimum COD removal (94%) at the frequency of 45 kHz (Yang et al. 2016) was obtained. Low frequency ultrasounds, i.e. 20-24 kHz were also sufficient for disinfection of treated wastewater or wastewater obtained by vegetable washing (Antoniadis et al. 2007, Anese et al. 2015).

Considering the technological aspect, there is a list of advantages resulting from the use of ultrasounds in excess sludge management, e.g. the breakage of extracellular polymeric substances and destruction of waste activated sludge cells (Liu et al. 2015), decomposition of organic compounds and formation of soluble substances (Zhuo et al. 2012, Parkitna et al. 2013) as well as the enhancement of the formation of short chain fatty acids (SCFA) with the dominance of acetic and propionic acids (Liu et al. 2014, Liu et al. 2015) and VFA (Zawieja et al. 2009). All these phenomena reduce the time of anaerobic digestion. Some authors shorten the range of frequency from 20 to 25 kHz for the processing of excess sludge (Zielewicz 2007). Hence, in the discussed study sonication applied to waste activated sludge pretreatment was carried out at the frequency of 20 kHz for 10-15 minutes (Yan et al. 2010, Liu et al. 2014, Liu et al. 2015). In the case of sunflower oil cake fermentation carried out at the same frequency, the processes were run from 16.6 to 331.2 minutes (Fernández-Cegrí V et al. 2012). In water degummed of soybean gum higher frequency equal to 28 kHz was used (Jiang et al. 2014).

The practical use of the sonication possesses many benefits, i.e. the efficient run of the process with no additional use of chemicals, the performance of the process at low/ medium temperature and pressure conditions, the possibility of installation hermetization, and the introduction of the sonication unit to the existing installation (Zielewicz 2007, Zielewicz and Tytła 2015). Also, the economic aspect of using ultrasounds on the industrial scale is important. The consumption of energy is given as per volume unit of wastewater/sludge [kWh/m³] (density of energy) or per unit of dry substance in sludge [kWh/kg d.w.] (specific energy) (Zielewicz-Madej and Sorys 2007). For those reasons the method is found to be environmentally friendly and the method is considered as green technology (Rokhina et al. 2009, Yan et al. 2010, Zielewicz 2007).

In the study, the possibility of using ultrasounds already in the wastewater pre-treatment stage was discussed. Although oily contaminants do not appear in municipal wastewater in as high amounts as in industrial wastewater, in the case of municipal wastewater treatment plants localized in tourist areas, especially during the high season, the use of additional treatment process in the form of sonication may significantly improve the operation of the plant as well as the quality of the purified stream. The preliminary treatment of synthetic wastewater by means of sonication is aimed to decompose oils. The process was observed by the formation of four long chain fatty acids (LChFA): palmitic, stearic, oleic and linoleic ones. The stream enriched in that acid was next introduced to high performance bioreactors.

Materials and Methods

Simulated municipal wastewater

SMW prepared from organic components: 0.32 g peptone/L, 0.22 g extract/L, 0.06 g urea/L, and mineral components: 0.056 g K_2 HPO₄/L, 0.014 g NaCl/L, 0.008 g CaCl₂×2H₂O/L and 0.004 g MgSO₄×7H₂O/L was used in the study. The components of the SMW were chosen according to the standard for biodegradation of organic compounds in water environment but their concentrations were modified (PN-EN ISO 11733). In order to determine the changes in the presence of fatty acids, the additional contamination was one type of edible oil – rape oil (popular grocery product widely used in Poland) which was introduced at a concentration of 0.02%.

Equipment and methodology

The study was carried out in 3L glass, cylindrical reactors to which oil and SMW were introduced. Two methods were used to introduce the oil into the water: conventional mixing (SMW+0.02%+mixing) and with using ultrasounds was (SMW+0.02%+ultrasounds). achieved Sonication at operating frequency of 35 kHz and ultrasonic time of 30 minutes (IS-5,5 InterSonic). Consumption of energy per volume unit of wastewater was 25 kWh/m3. In the study, the sonication process was run for a long time in order to obtain the emulsified solution of high stability. On the basis of non-public results of preceding studies on the change of TC and TOC in the sonicated sample it was determined that the stability of such emulsions reached the minimum of 24 hours.

Next, the reactors were placed on magnetic stirrer (IKA) and kept in thermostatic chamber (TermCon2, ELKAR) to provide constant working conditions. The temperature conditions, i.e. 15° C, 20° C and 30° C were applied during the whole experiment. The temperature in the thermostatic chamber was automatically kept constant with the accuracy of +/-0.1°C.

Sample analysis

The aim of the study was to determine the impact of mechanical mixing and sonication on the properties of SMW with oil component. The analysis of parameters of raw wastewater (0 h) and pre-treated wastewater (after 2, 4, 6, 24, 48 and 72 hours of

inoculation) was performed. The samples were collected from the cross section area of the reactor localized in the centre of the reactor. The studies included the analysis of the following chemical parameters: pH, COD and BOD_5 , long chain free fatty acids concentration.

The pH was measured with the use of pH-meter equipped (Elmetron) with glass electrode, which was degreased after every measurement series and checked with the use of standards of pH 4.00 and 7.00 (Avantor Performance Materials Poland S.A.).

The total concentration of organic compounds was assayed as COD and BOD_5 . COD assays were made using the photometer (Spectroquant Pharo 100, Merck). BOD_5 was measured manometrically using OxiTop vessels (OxiTop, WTW).

Determination of LChFA

The method for determination of LChFFA (as free fatty acids - FFA) in oily wastewater, extracted with dichloromethane, was developed (Łobos-Moysa and Dudziak 2011). The fatty acids were esterified using BF, in methanol solution (Sigma--Aldrich), then they were extracted with dichloromethane and analyzed using gas chromatography-mass spectrometry analysis Saturn 2100 T (Varian). The GC-MS was equipped with a SLBTM –5ms capillary column: 30 m \times 0.25 mm and film thickness of 0.25 µm (Varian). The following temperature was applied: from 80 to 280°C. Long chain acids (C8:0-C24:0) were used as single lipid and mix lipids standards (Sigma--Aldrich). Limit of aqua determination was in range from 6.3 to 35 $\mu g/L.$ In Fig. 1. the chromatogram of all possible acids formed during the process is shown. However, during the study the presence of four acids was followed up, due to their most common appearance in municipal wastewater, i.e. saturated acids: palmitic (C16:0), stearic (C18:0) and unsaturated acids: oleic (C18:1), linoleic (C18:2) (Łobos-Moysa et al. 2010).

Results and Discussion

The impact of various methods of oil mixing with wastewater on chemical parameters of SMW

The fats present in wastewater in the form of emulsion or a thin layer floating on the surface, may negatively impact not only microorganisms. Fats are not directly an easy substrate. However, properly pretreated wastewater may be a good source of carbon for microorganisms. SMW was evaluated as a useful substrate on the basis of COD, BOD₅ and LChFFA appearance in the temperature of 20°C.

The most significant change in wastewater chemical parameters after the introduction of oil was observed in the case of COD (Table 1). For SMW+0.02%+ mixing the slow increase in COD (930 mgO₂/L - 1062 mgO₂/L) within 24 hours of the process was observed. In the case of SMW+0.02%+ultrasounds the increase and the decrease of COD value (1163 mgO₂/L $-1202 \text{ mgO}_2/\text{L} - 1075 \text{ mgO}_2/\text{L}$) were observed in reference to the initial value. The increase was probably caused by fats ultrasonic hydrolysis and by the formation of soluble COD during wastewater moldering while the decrease was caused by the degradation of organic compounds, including oil, under the influence of the formed free radicals. The process occurred intensively in the case of SMW+0.02%+ultrasounds and the significant increase of COD is consistent with the literature i.e. the conversion of the suspended forms of both COD and BOD to soluble COD and BOD was observed (Nasseri et al. 2006). In this study, two frequencies: 35 and 130 kHz and three times of treatment: 10, 30 and 60 minutes were used. The phenomenon is also observed in the anaerobic digestion process of waste activated sludge (Zhuo et al. 2012).

After the first day, different phenomena were observed. In the case of mechanical mixing the thin layer of oil reformed on the wastewater surface (the decrease of COD value) and in the



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case of sonication the soluble organic compounds appeared (the increase of COD value) (Fig. 2). Both phenomena were determined on the basis of the appearance of four LChFFA.

The changes of COD were accompanied by the decrease of pH observed from 6.4 to 7.1 hour of the process for both reactors (Fig.3). The variations in pH of the investigated solutions had a similar tendency i.e. from 7.1 to 6.5 (for SMW+0.02%+ mixing) and 7.1 to 6.4 (SMW+0.02%+ultrasounds) and these changes were not as essential for the evaluation of both processes. This is consistent with the literature (Nasseri et al. 2006).

The impact of various methods of oil mixing with wastewater on the appearance of LChFFA in SMW

In biological method, wastewater is a nutrition solution which provides energy and growth nutrients to microorganisms. The biological treatment of oil compounds starts with enzymatic hydrolysis that removes the long chain fatty acids from the glycerol molecules of triglycerides. The final products in the aerobic conditions are carbon and water, whereas in the anaerobic one – carbon and methane.

The changes in acids concentrations observed in the reactors with SMW+0.02%+ultrasounds were referred to ones observed in the reactors with SMW+0.02%+mixing but changes were more intense in the first reactor (Table 1). The use of ultrasounds in pre-treatment of wastewater resulted in a significant increase of palmitic acid (from 48.3 to 93 μ g/L and 283.7 μ g/L in 24 hours). The use of sonication allowed to slow down the appearance of this acid (from 58.8 to 72.1 μ g/L and 92.3 μ g/L in 24 hours and only then 117 μ g/L in 72 hours) (Table 1). At that time, the second saturated acid – stearic acid was present in small quantities and it turned out to be too negligible for research.

Another phenomenon was observed in the case of unsaturated acids – oleic and linoleic acids reduce the concentration regardless of the method of mixing (Table 1). The biggest changes in free fatty acids concentration were observed for saturated acid – palmitic acid – and unsaturated acids – oleic and linoleic acids – after 24 hours. This is

analogous to disadvantageous phenomena which can occur during the production of edible oils, where sonication process is used, (Chemat et al. 2011) and their dewatering. Additionally, the difference in susceptibility of oils to quality worsening depending on its type was also observed. Sunflower and corn oils were found to be the most sensitive ones (Chemat et al. 2004). The study of the use of ultrasounds in oil extraction and bleaching of oil did not confirm the impact of the process on the oil quality including changes in the composition of fatty acids (Su et al. 2013).

The increase of COD, i.e. the formation of soluble organic compounds in wastewater did not correspond to the increase of the content of all investigated LChFA. As a result of sonication, during the first 6 hours of the process, the tendencies in the content of COD, palmitic and stearic acids were similar, while the increase of oleic and linoleic acids content was preceded with the COD content increase (Fig. 2, 4 and 5). The short-chain fatty acids (SCFA) were not the object of this study.

Ultrasounds were applied to various industrial wastewater pre-treatments (Adulkar and Rathod 2014, Oz and Uzun 2015). Studies of dairy wastewater pre-treatment with the use of the hydrolytic enzyme lipase and the ultrasounds showed the enhanced mass transfer, as well as boosting the rate of hydrolysis and lowering the reaction time (Adulkar and Rathod 2014). Similarly, the free LChFAs, appearing in this process, may be a substrate (source of carbon) for microorganisms. The presence of other carbon sources, e.g. glucose and nitrogen compounds or peptone, can positively affect the decomposition of oil and fats (Tano-Debrah et al. 1999).

The impact of oil mixing temperature on chemical parameters of SMW

After sonication the reactors were thermostated at various temperatures, i.e. 15°C, 20°C and 30°C. COD changed significantly at 20 and 30°C. However, at 15°C COD did not change significantly. In 20°C the increase of COD caused by decomposition of oils accompanied by the formation of soluble organic compounds on the surface was observed (Fig. 2). The

Chemical parameters			Time, h						
			0	2	4	6	24	48	72
COD, mg/L		ultrasounds	1163	1100	1215	1202	1075	1300	1400
		mixing	930	930	930	950	1062	932	810
pH ultrasound mixing		ultrasounds	7.0	7.1	7.1	7.0	6.9	6.4	6.8
		mixing	7.0	7.1	7.1	6.9	7.0	6.5	6.9
saturated	C16:0, µg/L	ultrasounds	48.3	64.0	92.6	73.7	43.0	283.7	482.7
		mixing	58.8	60.0	64.0	72.1	92.3	56.3	117.1
	C18:0, µg/L	ultrasounds	20.1	34.9	25.4	42.0	9.0	61.9	42.1
		mixing	40.5	30.1	39.5	28.1	35.2	30.1	41.8
unsaturated	C18:1, µg/L	ultrasounds	55.6	39.7	38.0	41.6	176.1	201.1	256.2
		mixing	64.5	38.7	49.5	44.7	130.0	44.8	109.5
	C18:2, µg/L	ultrasounds	36.7	26.3	34.0	32.8	163.1	156.0	182.7
		mixing	52.3	39.2	33.6	27.6	99.5	38.2	83.6

Table 1. Organic concentration and pH in temperature 20°C



biggest increase was observed in 48 hour. In 30°C, the soluble organic compounds were formed. These were the products of an early decay of oil that was caused by sonication and high temperature (the reactors were open, while the thermostatic cabinets were not hermetized). COD is an insufficient parameter to observe changes in wastewater properties. In the case of oil degradation, the local generation of very high temperature could also be important (Ramteke and Gogate. 2015, Rokhina et al. 2009). Next, keeping the reactors in thermostatic chamber at 30°C contributed to further degradation.

Variations in pH of investigated solutions had a similar tendency but different intensity (Fig. 3). The lowest values of pH were observed in the reactor kept at 30°C on the first day of the study, in the reactor kept at 20°C on the second day, and in the reactor kept at 15° C on the third day. It showed that for the proper preliminary treatment of oily wastewater sonication should also be accompanied by a proper process temperature i.e. 30° C.

The impact of oil mixing temperature on the appearance of LChFFA in SMW

After the sonication process the changes in the qualitative composition of wastewater treated at various temperatures occurred at different intensity depending on temperature, length of carbon chain and type of bonds (Fig. 4-7). The concentration of saturated acids i.e. palmitic acid (C16:0) and stearic acid (C18:0) slowly increased to 353-483 µg/L and 42–57 µg/L, respectively (Fig. 4 and 5). For unsaturated acids, i.e. oleic (C18:1) and linoleic (C18:2) ones the decrease of concentration was noted already in the first several hours of the process performance (Fig. 6 and 7). Then, in 30°C a drastic increase in the concentration of both acids was observed - to value 486 µg/L (C18:1) and 428 µg/L (C18:2), respectively. This is analogous to oil degradation (oil rancidity) occurring in grocery products that are badly stored. The temperature and light are the main conditions that affect this process (Wroniak et al. 2015). The unsaturated acids (oleic (C18:1) and linoleic



Fig. 2. The impact of temperature on COD



Fig. 3. The impact of temperature on pH

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acids (C18:2)) are more susceptible to oxidation (Cichosz et al. 2011, Konratowicz-Pietruszka 2013). The appearance of free unsaturated acids took a considerable amount of time. The reverse was true for palmitic acids (C16:0) (Fig. 4). Stearic acid proved not to be a very essential acid.

Similarly, as in the case of COD, the general indicator of organic compounds content, also of specific organic contaminants, the temperature was found to be an important factor in the oily wastewater treatment process. However, the use of sonication in a municipal wastewater treatment plan as a process preceding the biological treatment by means of an activated sludge method in cooler climate zones may be economically unjustified. On the other hand, sonication can be used in the case of industrial wastewater contaminated with significant amounts of oils and it can be profitable. For example, the studies on the use of ultrasounds before anaerobic fermentation carried out at pH 10 and in the temperature range from 10 to 55°C can be mentioned (Zhuo et al. 2012). The optimal temperature was found to be at the level of 37°C. However, also in this process, run at the temperature of 20°C, the amount of formed short chain fatty acids was found to be the result of sonication pretreatment rather than hydrolysis process (Liu et al. 2014).

Conclusions

- 1. The studies showed the usefulness of ultrasounds in pretreatment of wastewater containing oil, e.g. both COD and LChFFA: palmitic, stearic, oleic and linoleic acids, because of:
 - a) oil degradation and increase of soluble COD value,
 - b) increase in the rate of hydrolysis that removes the long chain fatty acids from the glycerol molecules of triglycerides,
 - c) (a)+(b) appearance of the substrate for the biological reaction.
- 2. The next step of wastewater treatment may be a biological treatment. The ultrasound aided process may allow to



Fig. 4. The impact of temperature on appearance of palmitic acid (C16:0)



Fig. 5. The impact of temperature on appearance of stearic acid (C18:0)



Fig. 6. The impact of temperature on appearance of oleic acid (C18:1)



Fig. 7. The impact of temperature on appearance of linoleic acid (C18:2)

boost the rate of hydrolysis and lower the biological treatment time. LChFFA may be an easy source of carbon for microorganisms. The observed changes in the quality of synthetic wastewater after the introduction of edible oils are advantageous for their biological treatment. However, in reference to changes observed in municipal wastewater, all processes occurred at a slower pace.

- 3. Sonication as a pre-treatment influenced the appearance of acids in wastewater in different ways. Differences were observed between saturated (palmitic (C16:0), stearic (C18:0)) and unsaturated (oleic (C18:1), linoleic (C18:2)) acids.
- 4. The initial wastewater moldering and its sonication can also be recommended as it improves the efficiency of biological treatment of municipal and industrial wastewater. The parameters, which were not optimized during this study, were the frequency and time. The optimal parameters of pretreatment, i.e. frequency, specific energy, sonication time

and temperature should always be determined individually for a given type of wastewater before the start of the process.

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ZASTOSOWANIE DEZINTEGRACJI ULTRADŹWIĘKOWEJ DO PODCZYSZCZANIA ŚCIEKÓW ZAOLEJONYCH

Streszczenie: Celem badań było określenie wpływu sposobu mieszania oleju ze ściekami na właściwości syntetycznych ścieków komunalnych zawierających olej jadalny (SŚK+0,02% w/v oleju rzepakowego). Badania były prowadzone w szklanych reaktorach o objętości 3 litrów, do których wprowadzano ścieki SŚK+0,02%. Zastosowano różne metody mieszania: mechaniczne mieszanie (SŚK+0,02%+mieszanie) oraz dezintegrację ultradźwiękową (SŚK+0,02%+ultradźwięki). Ścieki były poddane dezintegracji ultradźwiękowej z częstotliwością 35 kHz przez 30 minut. Podczas badań utrzymywano stałą temperaturę (15°C, 20°C oraz 30°C). W celu określenia efektywności metody mieszania, ścieki surowe oraz oczyszczone – po 2, 4, 6, 24, 48 i 72 godzinach inkubowania poddano analizie (pH, ChZT, BZT₅, zawartości długołańcuchowych kwasów tłuszczowych).

Najbardziej istotne zmiany w parametrach ścieków po dodaniu oleju obserwowano dla wskaźnika ChZT. W przypadku ścieków SŚK+0,02%+mieszanie obserwowano powolny wzrost ChZT w ciągu 24 godzin. W przypadku SŚK+0,02%+ultradźwięki stwierdzono wzrost i następnie spadek ChZT. Zmiany stężenia kwasów obserwowane w reaktorach zawierających SŚK+0,02%+ultradźwięki były podobne do zmian w reaktora z SŚK+0,02%+mieszanie, przy czym bardziej intensywne zmiany były w pierwszym przypadku. Zastosowanie dezintegracji ultradźwiękowej do podczyszczania ścieków skutkowało intensywnym pojawieniem się kwasu palmitynowego w pierwszych 6-ciu godzinach. Niezależnie od sposobu mieszania (mechaniczne mieszanie lub dezintegracja ultradźwiękowa) stężenie kwasów oleinowego i linolowego malało. Największe zmiany w stężeniu wolnych kwasów tłuszczowych obserwowano dla kwasów: palmitynowego, oleinowego i linolowego po 24 godzinach.