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Effect of pre-treatment and conditions on the appearance of long chain fatty acids in treatment of wastewater containing oil

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ABSTRACT

The aim of the research was to increase the efficiency of treatment of wastewater containing edible oil. In order to increase the bioavailability of this wastewater, ultrasound method was proposed, as a pre-treatment of wastewater before the biological treatment. An emulsification oil in wastewater by ultrasound has initiated the process of oil hydrolysis and resulted in the appearance of free fatty acids in the water phase (saturated acids: palmitic, stearic; and unsaturated acids: oleic, linoleic). Degradation of oil and the formation of dissolved substrates were also favoured by the application of elevated temperature of 30°C. While at the temperature of 15°C, the oil emulsion maintained its stability through the first hours of the research. The effectiveness of the treatment was compared on three types of wastewater: wastewater containing edible oil (0.1% + wastewater), wastewater containing oil changed by ultrasound (0.1% + ultr + wastewater) and wastewater which also contained other organic compounds (peptone and meat extract, urea, sodium acetate and starch) apart from oil (0.1% + ultr + wastewater). The introduction of co-substrate caused a decrease in the frequency of unfavourable phenomena in system – outflow of activated sludge.

Keywords: Edible oil; Fatty acids; Pre-treatment; Ultrasound; Activated sludge; Co-substrates

1. Introduction

Wastewater containing oil and grease substances (O&G) are mainly produced in various food industries, but O&G are also one of the most common substances in municipal wastewater. In this case, O&G come from households (fat and edible oil), catering establishments (edible oil), public buildings and industry. These pollutions are present in wastewater in the unchanged and changed form, for example, with detergents or after thermal treatment. O&G are present in the non-emulsified form, that is, the floating oil layers on the water surface and in the form of emulsions – oil drops in water. Regardless of the origin of wastewater, all are characterized by the tendency to cling to objects they come in contact with. This causes problems with the operation of the sewage system [1–4] and the mechanical–biological wastewater treatment plant [3,5]. It generates operational and maintenance cost [3].

Typical methods of removal of O&G are: gravity separation [6–8], flotation and dissolved air flotation [3, 9,10], coagulation and sedimentation [6,8], sorption onto mineral and organic sorbents [6,8] and membrane separation [8,11]. In the case of O&G floating on the surface of wastewater, such pollutants are easily removed by gravity separation as the primary treatment. Similarly, dissolved air flotation and separation are used. Microbubble air flotation [9], electroflotation [6], electrocoagulation using aluminium or iron electrode [7,8], sorption on regranulated cork granules and change of chemical conditions of wastewater [6] are counted as modification methods to increase efficiency. This O&G removal could be used successfully as the secondary step because of high removal efficiency. However, hazardous

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waste is produced in all of these methods. Another solution for this problem is biodiesel production from used oil [3].

So far, the biological treatment appears to be the cheapest method, but it also requires some pre-treatment. The type of primary treatment or both steps depends on the presence of pollutant in oily wastewater. Part of O&G which is not subject to biodegradation must be removed by physicochemical treatment – coagulation/flocculation followed by sedimentation/flotation [8,12]. In the case of phenolic compounds (olive oil mill wastewater), the photo-Fenton process or electrocoagulation with photo-Fenton process could be applied to high degradation of organic matter [8,13,14]. The short chain carboxylic acids present in the treated wastewater are non-toxic and biodegradable [13]. Water could be used for irrigation or disposal by sewer system for its treatment on urban wastewater treatment plant [14]. In highly efficient processes, water is reused [8].

The aim of the study was assortment of adequate pre-treatment of wastewater containing oil to change their properties and to minimize their negative impact on activated sludge.

2. Materials and methods

2.1. Methodology and equipment

Two stages of the research were carried out in the batch systems (part 1) and flow systems (part 2). During first part, two methods of pre-treatment as a changing the edible oil properties were used: addition of sodium hydroxide (NaOH) or ultrasound. NaOH was added at a selected dose up to 0.2 g/L. On the basis of own studies, ultrasound technique was applied at the following operating parameters: frequency of 35 kHz and time of 30 min [15]. This stage of the research was carried out in the batch systems with the 1 L volume in order to assess the effects of both methods. The equipment includes a magnetic stirrer (IKA, Germany) and a thermostatic chamber (TemCon2, ELKAR, Poland). The prepared oil (0.1%) in glass reactors was mixed and kept at a constant temperature, that is, 15°C, 20°C or 30°C during the whole experiment. The temperature was automatically kept constant with the accuracy of ±0.1°C.

The flow systems were comprised of a bioreactor and secondary sedimentation tank (total volume 15 L). Wastewater was transported to the bioreactor at a constant flow rate maintained by the pump (Verderflex). The treated wastewater and activated sludge were carried off the bioreactor by gravitational outflow, than collected in the secondary tank. In the end, treated wastewater flowed into final tank. Simultaneous aeration and stirring of the activated sludge in the bioreactor was carried out using air pumps. At this stage of the research, the synthetic wastewater was added to the edible oil as a co-substrate. This wastewater contained 0.34 g/L enriched broth, 0.25 g/L starch, 0.05 g/L sodium acetate, 0.03 g/L urea and mineral compounds. COD in raw wastewater was 2,300 mg/L and pH was 7.5 (on average).

2.2. Analytical methods

Organic compounds in the raw, pre-treated and treated wastewater by biological method were analyzed using a spectrophotometer (Pharo 100, Merck, Germany) as a the total concentration of organic compounds – COD and using a gas chromatograph (Saturn 2100 T, Varian Inc., Poland) as the specific component – free fatty acids in the aqueous phase (FFA). The fatty acids were esterified using BF_3 in methanol solution, extracted with dichloromethane and analyzed using gas chromatography – mass spectrometry analysis [15]. Limit of aqua determination was in range of 6.3–35 μg/L.

The pH was measured with the use of pH meter equipped (Elmetron, Poland) with glass electrode, which was degreased after every measurement series. The temperature and oxygen concentration in bioreactor were also measured using Elmetron equipment. The dry weight of activated sludge (MLSS) was determined at 105°C.

3. Results and discussion

3.1. Changing the properties of wastewater as a pre-treatment

In order to increase the bioavailability of wastewater contaminated with oil substances, addition of NaOH or use of ultrasound were proposed, as a pre-treatment of wastewater before the biological treatment. Examples of the application of surfactants are described in the literature, which contribute to the emulsification of oils or KOH and NaOH, which in the saponification reaction increase their bioavailability. In case municipal waste from restaurant traps, saponification of glycerides and fatty acids mixture produces fatty acids salts with surface-active properties [16]. It improves biological treatment under aerobic conditions. However, transesterification reaction can be used for production of soap, and thus for the recovery of raw materials from olive mill wastewater [17]. The application of the first method did not bring satisfactory results, that is, oil appeared in the form of floating layers on the surface of wastewater. Further research was carried out on ultrasound method.

The developed analytical procedure enabled the separation and identification of 12 fatty acids, but 4 fatty acids were determined in municipal raw wastewater, as well as treated wastewater, collected at each stage of the municipal treatment plant, that is, palmitic acid, stearic acid (saturated acids) and oleic acid, linoleic acid (unsaturated acids) [18].

The impact of using the unitary operation – pre-treatment of oily wastewater with ultrasound applied on their properties – was determined based on the analysis of raw and treated wastewater including the chemical parameters, that is, pH, as well as FFA content, and then the results were evaluated in terms of changes in the wastewater properties (Figs. 1–6). After applying ultrasound, the samples were incubated at temperatures of 15°C and 20°C (temperatures characteristic for municipal wastewater in Poland during winter and summer periods, respectively) and at elevated temperature, meaning 30°C, for the period of 24 h.

Based on research on various methods of 0.02% oil mixing with wastewater, the direct effect of ultrasound applied on pH was not found [15]. This is consistent with the literature regarding wastewater and sewage sludge [19]. Changes in pH occurred over time.

Oil emulsion maintained its stability through the first hours of the research at the temperature of 15°C (Figs. 1 and 4).

The decrease and then increase in FFA content in the aqueous phase (in the first place of unsaturated acids: oleic

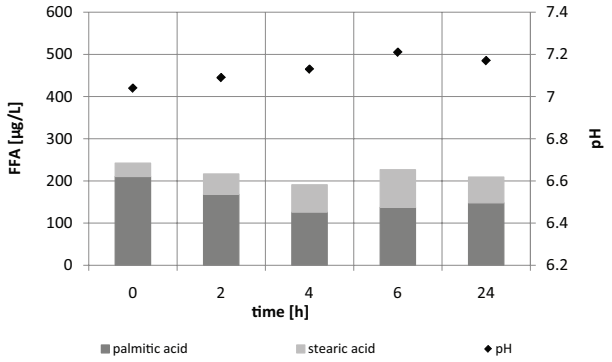

Fig. 1. Appearance of saturated acids and pH in wastewater after the ultrasound method at 15°C.

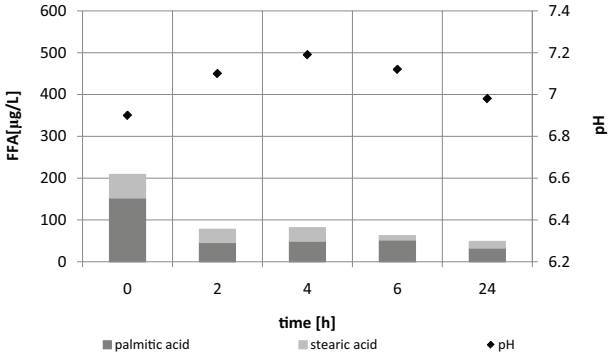

Fig. 2. Appearance of saturated acids and pH in wastewater after the ultrasound method at 20°C.

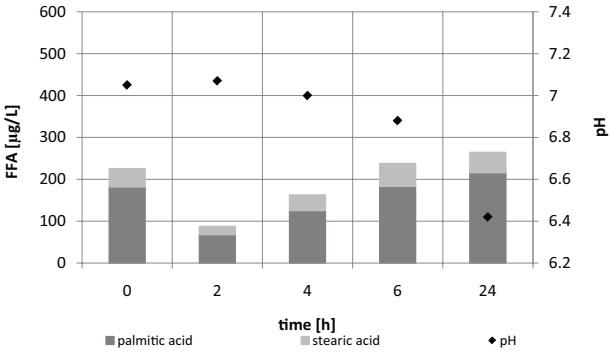

Fig. 3. Appearance of saturated acids and pH in wastewater after the ultrasound method at 30°C.

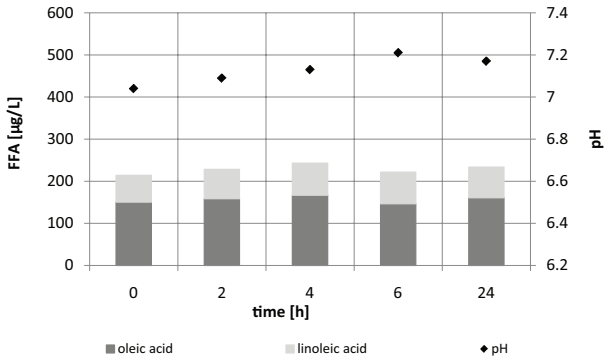

Fig. 4. Appearance of unsaturated acids and pH in wastewater after the ultrasound method at 15°C.

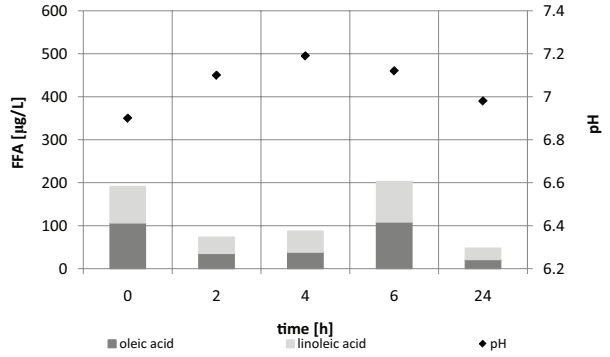

Fig. 5. Appearance of unsaturated acids and pH in wastewater after the ultrasound method at 20°C.

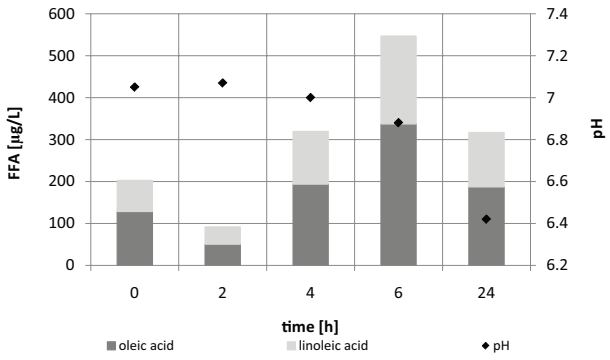

Fig. 6. Appearance of unsaturated acids and pH in wastewater after the ultrasound method at 30°C.

and linoleic acids, and then saturated acids: palmitic and stearic acids) showed the changes in the wastewater properties at 20°C (Figs. 2 and 4) and at 30°C (Figs. 3 and 6). The biological wastewater treatment is the elimination of organic substrates by microorganisms. Edible oils contained in the wastewater, which are water-insoluble organic substances, cannot directly be the substrate for bacteria of the activated sludge. Bacteria could use organic compounds as a substrate, these compounds must be in dissolved form. Enzymatic hydrolysis of oils is carried out in the extracellular manner, which allows the distribution of triglycerides to glycerol and free fatty acids (one molecule of glycerol and three molecules of fatty acids are formed). Hence, these long chain fatty acids appear in the water phase. The pre-treatment of oily wastewater could be done by ultrasound method.

Degradation of oil and the formation of dissolved organic compounds in the samples subjected to ultrasound were also favoured by the application of elevated temperature of 30°C (Figs. 3 and 6). In these samples, the significant variation in FFA concentrations (decrease then increase) and the significant decrease of pH was observed.

The pre-treatment of wastewater with using of ultrasound has initiated the process of oil hydrolysis and resulted in the appearance of free fatty acids in the water phase. The palmitic and stearic acids in vegetable oils are found in triglycerides, which are non-polar lipids. As insoluble in water, they do not undergo hydrolysis, as the lipases work properly in the well-dispersed emulsion [20]. In another form, they can cause slower biodegradation [21]. The proposed method of ultrasonic hydrolysis for emulsifying wastewater containing oil substances has contributed to the bio-availability of oils, that is, to the emergence of substrates for microorganisms of the activated sludge, thus contributing to the shortening of wastewater treatment time. The literature data shows that the occurrence of emulsified oil substances in wastewater does not have a negative effect on biodegradation under aerobic conditions, nor does it reduce the rate of oxygen consumption [22].

3.2. Effect of pre-treatment on biological treatment by activated sludge method

The course of wastewater treatment with biological methods and its effectiveness are dependent on a number of operating parameters, for example, on the content of activated sludge in the bioreactor, the load of the activated sludge to the substrate (F/M), the hydraulic retention time (HRT), the degree of recirculation of the sludge, as well as on the conditions of the process, for example, the temperature, pH, oxygen concentration, the mount of nutrient substances, the susceptibility of the compounds to biodegradation and the occurrence of toxic compounds which are difficult to biodegrade.

Providing the right conditions, the activated sludge method is cost-effective. In these studies, it was observed how a change in the oil properties can affect the wastewater treatment by activated sludge. Two types of wastewater were used, that is, wastewater containing edible oil (0.1% + wastewater) and wastewater containing oil changed by ultrasound (0.1% + ultr + wastewater). Operational parameters of the systems are shown in Table 1.

The efficiency of treatment by activated sludge of wastewater as COD in outflow is shown in Fig. 7. In the case of 0.1% + wastewater, the study lasted only 23 d. During this time, two system failures occurred (9 d and 23 d) and COD in the outflow was 361 and 327 mg/L, respectively. Small increase in biomass was also noted. Probably, oil substances by covering the flocs of the activated sludge prevent the exchange of substrates and products at the phase interface, including the inability of oxygen accessing microorganisms, resulting in the decreased aerobic efficiency.

Table 1
Operational parameters of systems

Parameters/systems	0.1% + wastewater	0.1% + ultr + wastewater	0.1% + ultr
F/M, gBOD_5/g·d	0.8	0.6–0.8	0.8
HRT, h	11	10.5	10
pH	7.5	7.5	7.0
Temperature, °C	20	20	20

In the case of 0.1% + ultr + wastewater, fluctuations in COD value were also observed (i.e., 122–440 mg/L (1–14 d) and then decrease 380–82 mg/L (16–41 d)), but overall, COD in treated wastewater was between 129 and 160 mg/L and from 30 d of research, the bioreactor worked well. The concentration of microorganisms in the biorector increased. From the moment of stabilization, measured ratio F/M was 0.6.

Treatment of industrial wastewater containing high levels of fat is especially important before entering into the pipes of the sewage systems. The relationship between the chemical properties of O&G deposits was determined, that is, deposit weight was increased at higher oleic acid contents [4].

3.3. Effect of co-substrates nutrient on oily wastewater treatment

Another factor taken into account was the composition of wastewater. Two types of wastewater were used in this study: wastewater containing only edible oil (0.1% + ultr) and the wastewater containing other organic compounds (peptone and meat extract, urea, sodium acetate and starch) apart from oil substances (0.1% + ultr + wastewater). The efficiency of treatment by activated sludge of these two types of wastewater as COD in outflow is shown in Fig. 8. In the case of first wastewater, the oil being the only source of carbon was not a substrate accessible to all organisms, and its biodegradation had to be preceded by the enzymatic hydrolysis. COD range 86–105 mg/L in treated wastewater (0.1% + ultr), but system was characterized by emergency work. The biomass was washed out, which also resulted in a very slow increase in MLSS concentration in activated slugde system (Fig. 8). For these reasons, the study lasted only 21 d.

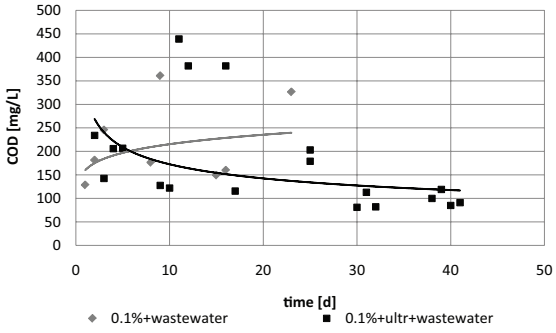

Fig. 7. Effect of wastewater pre-treatment on COD in wastewater treated by activated sludge.

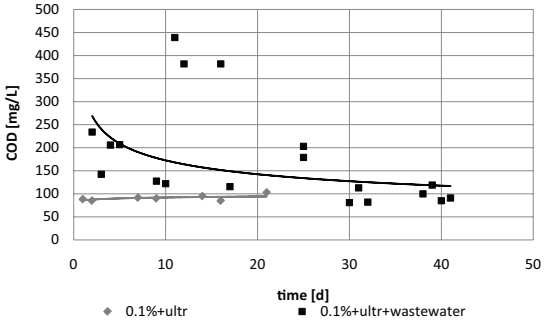

Fig. 8. Effect of wastewater pre-treatment and co-substrate adding on COD in wastewater treated by activated sludge.

It was different in the second case probably the additional substrates were first used as the carbon source, while the oil hydrolysis followed at the same time, so the resulting fatty acid could undergo further biodegradation. Municipal wastewater is treated as a nutrient solution, from which the activated sludge microorganisms collect substances that correspond to their life needs. The system of wastewater containing vegetable oils can therefore affect their biodegradation.

Similarly, good results were obtained during anaerobic co-digestion of fats, oil and grease with municipal sludge [23]. According to the literature, stimulation of aerobic treatment of wastewater containing oil can be achieved by suitable conditions, for example, through pH correction or the implementation of biodegradation under thermophilic conditions [24]. In the case of wastewater from production of refined edible oil which was characterized by high temperature, this is possible. The delivery of co-substrates or the application of commercial bio-preparations directly in the sewage system will be conducive to increasing the efficiency of the treatment in order to increase the biodegradable COD fraction on the inflow to the wastewater treatment plant [25]. Replacing wastewater containing oil with minerals such as phosphates does not always have a positive effect [26]. The oil degradation is also supported using bioaugmentation [27].

4. Conclusion

The aim of the work was the intensification of biological processes for the treatment of wastewater containing oil, by introducing the initial sonication of oil as pre-treatment and by addition of co-substrates as the carbon source.

Comparing the nature and speed of changes in time of the physical and chemical parameters of the wastewater, it was found that the application of ultrasound has a greater effect on changes of properties of wastewater. The pre-treatment of wastewater containing oil by this method has initiated the process of oil hydrolysis and resulted in the appearance of substrate in the water phase. The occurring phenomena were the decrease and increase in four FFA concentrations (saturated acids: palmitic, stearic and unsaturated acids: oleic, linoleic). Degradation of oil and the formation of dissolved substrate subjected to ultrasound were also favoured by the application of elevated temperature of 30°C.

The second important factor was the introduction of organic co-substrates: enriched broth, starch, sodium acetate, urea and mineral compounds. Oil being the only source of carbon was not a substrate accessible to all organisms. Its biodegradation has to be preceded by the enzymatic hydrolysis.

In conclusion, the use of pre-treatment of wastewater caused the ultrasonic hydrolysis of vegetable oil, and therefore the availability of FFA for microorganisms. Thanks to the co-substrate, the easily accessible carbon source was introduced. Further improvement of biological treatment can thus be to the maintenance of optimal conditions, that is, under thermophilic conditions (at 30°C).

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