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Biodegradation of wastewater components causing O&G deposits formation in sewers

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ABSTRACT

The aim of the research was to compare the degree of biodegradation of oil contaminants present in municipal wastewater in dependence of the type of pollutants. Occurrence of oil contamination, free fatty acids (FFA) (as a result slow chemical hydrolysis of oil), and metallic soaps (as a saponification process with FFA) in wastewater may cause deposits on the walls of pipes and infrastructure. In this study, sodium acetate (CH_3OONa), sodium salts of fatty acids: sodium oleate ($C_{18}H_{33}OONa$), sodium stearate ($C_{18}H_{35}OONa$), and oily wastewater were used as exemplary substrates. Sodium acetate as a single substrate and oily wastewater were similarly biodegradable: 92.6%–95.9% (the chemical oxygen demand (COD) reduction) and 91.2%–96% (COD reduction), respectively. Lower efficiency at the beginning of the process was observed for sodium oleate and sodium stearate as single substrates: 88.1%–97.2% and 86.3%–96.1% of COD reduction, respectively. In the case of wastewater, COD removal was obtained at a similar level: 91.2%, 91.2%–89.6%, but four main fatty acids (palmitic ($C_{16}H_{31}OOH$), oleic ($C_{18}H_{33}OOH$), linoleic ($C_{18}H_{31}OOH$), and stearic acid ($C_{18}H_{35}OOH$)) were removed at various efficiencies, depending on the acid type (the length of the carbon chain and number of double bonds).

Keywords: Edible oil; Fat; Sodium oleate; Sodium stearate; Oleic acid; Stearic acid; Deposit; Biodegradation

1. Introduction

Oil and grease substances (O&G) are one of the most common substances detected in municipal wastewater. O&G come from households (fats and edible oil), catering establishments (edible oil), public buildings, and industry. These substances are present in the wastewater in the nonemulsified form as the floating oil layers on the wastewater surface, and in the form of emulsions – oil droplets in water (different emulsion drop size distributions). Oily wastewater characterizes with the tendency to cling to objects it comes in contact with. This causes problems with the operation of the sewage system, and the municipal mechanical–biological wastewater treatment plant (WTP).

Problems with the operation of the sewage system arise from: using the waste disposers installed under a kitchen sink, that discharge the wastes to the sewer system [1], increase of O&G consumption – increase levels of O&G used in kitchen practices and disposed into the sewer system [1,2]. O&G are present in wastewater in the unchanged form (e.g., edible oil) and changed form (e.g., as a result of reaction with detergents or after thermal degradation). The compounds present in the cooking oil (and thus in wastewater) are mainly long and short fatty acids, esters of carboxylic acids, poly-aromatic hydrocarbons, and lactones [3,4].

O&G deposits reduce sewer diameters and can completely block pipes [2,5]. The formation mechanism of deposits in sewers is complex and includes: the cooling of frying oils deposition [1], the occurrence of free fatty acids (FFA) and their appearance as a result of slow chemical hydrolysis [5], metallic soap deposition (as a saponification process involving mainly calcium and FFA) [1,2,5,6], and as a consequence,

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the presence of other solid waste in wastewater, which also stick to the walls of pipes. Moreover, the formation of deposits is favored by concrete corrosion [5].

The fatty acid profiles for sewer deposits show that acids with chain length from C_{16} to C_{18} are most common [2]. Palmitic acid ($C_{16}H_{31}OOH$), oleic acid ($C_{18}H_{33}OOH$), and linoleic acid ($C_{18}H_{31}OOH$) dominate in these profiles [2,5,6], as well as in municipal wastewater [7]. The literature data show that palmitic and oleic acids present in wastewater cause higher deposits formation and accumulation than lauric and linoleic acids [8].

Similarly, as some organic compounds may play an important role in the mechanism of the deposits formation, the same is in the case of mineral compounds. Ca, Na, K, Fe, Al, and Mg are most common deposits components [2,9]. Calcium is the most dominate cation [1,2,6], and calcium concentration in deposits increases with water hardness [2]. Other studies show that calcium can be released from concrete surface at low pH conditions [5]. In addition to FFAs and fatty acid metal salts, deposits may also contain triacylglycerols, diacylglycerols, and monoacylglycerols [9]. Another hazard resulting from the deposits presence in pipelines is the formation and accumulation of biogas [10].

In the mechanical part of the WTP, O&G settle on the grates and walls of open channels and devices, creating a sludge, which is associated with odor release (mainly due to the formation of aldehydes and volatile fatty acids) [11]. In the biological part of the treatment plant, in addition to the phenomenon of the formation of deposits on the reactors walls, fats and oils affect the operation of the activated sludge [12].

In order to reduce the impact of oil pollution on the sewage system and WTP, two strategies can be proposed. The most important is the prevention based on installation of efficient grease interceptors [8] or collectors, also in households [13]. Then, oil pollution can be used as a valuable resource in energy production [13,14], and the utilization paths are conversion to biodiesel, direct combustion in a cogeneration plant and the production of biogas at agricultural biogas plants [13].

The second solution may be to shorten the sewage system, and apply WTP, that is, membrane bioreactor (MBR) in the vicinity of sources of oil and fat contamination. The advantages of MBR include compactness, small size, and the easy extension of the plant – increasing membrane surface.

The aim of this research was to compare the rate of biodegradation of oil contaminants present in municipal wastewater. It was found that these components in particular caused the formation of deposits on the walls of pipes and at the infrastructure of WTP. However, highly efficient biodegradation of domestic wastewater will depend on the innovativeness of biological methods, because oil contaminants are not completely removed in WTP and can enter the natural receiver.

2. Materials and methods

2.1. Synthetic wastewater

In the first stage, synthetic wastewater containing single compound: sodium acetate (CH_3OONa) (Avantor Performance Materials Poland), sodium oleate ($C_{18}H_{33}OONa$) (Sigma-Aldrich Sp. z.o.o, Poland), sodium stearate ($C_{18}H_{35}OONa$) (Sigma-Aldrich Sp. z.o.o, Poland), was prepared. The sodium acetate was a comparative ingredient. COD in raw wastewater was 1,039 mg L^{-1} (CH_3OONa) and 1,013 mg L^{-1} ($C_{18}H_{33}OONa$ and $C_{18}H_{35}OONa$).

In the second stage of the research the synthetic wastewater was mixed with the edible oil – rapeseed oil (0.03% v/v oil emulsion) as a cosubstrate. The synthetic wastewater contained organic compounds: 0.16 g L^{-1} peptone (PEPTOBAK S-0009, BTL, Poland), 0.11 g L^{-1} enriched broth (P-0022, BTL, Poland), 0.03 g L^{-1} urea, and mineral compounds: 0.028 g L^{-1} K_2HPO_4, 0.007 g L^{-1} NaCl, 0.004 g L^{-1} $CaCl_2 \times 2H_2O$, 0.002 g L^{-1} $MgSO_4 \times 7H_2O$. The enriched broth was a culture broth with an additional dose of peptone for microorganisms. Rapeseed oil was sonicated at 35 kHz [15] and then oil was mixed with synthetic wastewater. COD in raw, synthetic wastewater was 1,200 mg L^{-1} and pH was 7.0 (on average).

2.2. Methodology and equipment

The biodegradation of four synthetic wastewater was carried out in the batch system – in 3 L glass, cylindrical bioreactors. The equipment included magnetic stirrers (IKA) and aeration pumps (HAILEA). The bioreactors containing wastewater and activated sludge were placed on magnetic stirrers and maintained under aerobic conditions at ambient temperature. Table 1 shows the operating parameter of bioreactors. The activated sludge was collected from the municipal WTP and contained bacteria of protozoan group (e.g., *Ciliata*) and aquatic animals (e.g., *Rotatoria*). In the first stage, biomass content was used at the level of 3.6–4.2 g L^{-1}. Thus, wastewater treatment was carried out at low F/M. In the second stage, much lower biomass content was applied.

The physicochemical analysis of raw wastewater (0 h) and wastewater treated by biological method (after 1, 2, 3, and 4d of inoculation) was performed. Organic compounds were analyzed using a spectrophotometer (Pharo 100, Merck KGaA, Germany) as a total concentration of organic compounds – COD_{Cr} and using a gas chromatograph (Saturn 2100 T, Varian Inc., CANDELALAB Sp. z.o.o, Poland) for determination of the specific components. Oleate, stearate, and fatty acids were esterified using BF_3 in methanol solution (Sigma-Aldrich Sp. z.o.o, Poland), extracted with dichloromethane and analyzed as methyl derivatives using GC-MS [16]. Limit of determination of FFAs in aquatic environment was in range from 6.3 to 35 μg L^{-1}.

Table 1
Operating parameters of bioreactors

Parameters/ wastewater	Single component: C_2H_3OONa $C_{18}H_{33}OONa$ $C_{18}H_{35}OONa$	Mixed wastewater 0.03% (rapeseed oil) + substrate (synthetic wastewater)
F/M (g COD g^{-1} d^{-1})	0.12–0.15	0.17–0.65
Initial biomass concentration (g L^{-1})	3.6–4.2	0.9–3.6
HRT (d)	1; 2; 3; and 4	1 and 3
Temperature (°C)	18–21	18–21
Oxygen condition	Aerobic	Aerobic

The pH, temperature, and oxygen concentration in bioreactor were measured with the use of pH-, T-, oxygen-meter equipment (CX, Elmetron, Poland). A biomass concentration was expressed as a dry weight of activated sludge (MLSS).

3. Results and discussion

3.1. The biodegradation of sodium salts of fatty acids

In this study, sodium salts of fatty acids were used, that is, sodium oleate ($C_{18}H_{33}OONa$) and sodium stearate ($C_{18}H_{35}OONa$), because of their greater solubility than fatty acids solubility, and because of greater solubility of sodium salts of fatty acids than calcium and magnesium salts of fatty acids [17]. The sodium acetate (CH_3OONa) was a single, comparative ingredient in the biodegradation process. The mixed wastewater (0.03% rapeseed oil and synthetic wastewater) played the same role – it was a comparative wastewater in the biodegradation process, but as a set of fatty acids. The effectiveness of the process was assessed based on the COD removal (Fig. 1), and oleate and stearate removal (Figs. 2 and 3). Sodium acetate and synthetic wastewater were biodegraded with similar efficiency. Removal of COD was found at 92.6% and 91.2% (1d), 95.8% and 96.7% (3d), 95.9% and 96% (4d), respectively (Fig. 1). Sodium acetate is simple, organic substrate. Similar efficiency was achieved by combining oil pollution (rapeseed oil) with a more available carbon source (peptone, enriched broth, and urea) for activated sludge. Lower initial efficiency of the process was observed for sodium oleate and sodium stearate – 88.1% and 86.3% (1d), 89.5% and 89.4% (2d), 92% and 93.2% (3d), 97.2% and 96.1% (4d), respectively.

Comparison of COD removal with sodium oleate removal, and COD removal with sodium stearate removal showed that sodium oleate as a salt of unsaturated acid was degraded to a higher extent, that is, 98.9% (1d) than sodium stearate – a salt of saturated acid – 95.3% (1d) (Figs. 2 and 3). Despite the 100% degradation of these salts (2d), products of their biodegradation still remained in the wastewater. In the following days a further increase in COD removal was observed, that is, 89.5%–97.2% and 89.4%–96.1%.

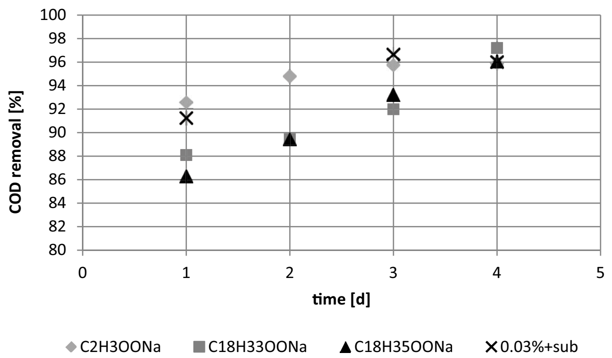

Fig. 1. COD removal during four wastewater treatment in aerobic condition and F/M = 0.12–0.17 g COD g^{-1} d^{-1}.

3.2. The biodegradation of fatty acids

During the tests, 0.03% oil emulsion and synthetic wastewater were introduced into the bioreactors. The course of wastewater treatment with biological methods and its effectiveness depend on a number of operating parameters, that is, the load of the activated sludge with the substrate (F/M) and the hydraulic retention time (HRT), as well as on the conditions of the process, that is, the amount of nutrients and the susceptibility of the compounds to biodegradation. Using F/M ratio from 0.17 to 0.65 g COD g^{-1} d^{-1} the following COD removal was obtained: 91.2%, 91.2%, 90.7% and 89.6% (Figs. 4–7).

Another phenomenon was observed in the case of FFA. Oil is not directly available and simple substrate for microorganisms. Triglycerides in the presence of a lipase are hydrolyzed to glycerol and FFA. Therefore, these acids appear in the water phase. Under aerobic condition, biodegradation of fatty acids by β-oxidation involves splitting off two-carbon fragments and forming intermediate products, that is, acids with chains shorter by two atoms of carbon and acetyl-CoA. The final products of degradation are CO_2 and H_2O. Thus, FFA found in the treated wastewater, cannot be considered just as a substrate that degrades during the biodegradation, but also as a product. At this stage of study, oily water pretreatment was applied using ultrasounds [15]. The rate of hydrolysis increased, that is, long chain fatty acids were released from the glycerol molecules of triglycerides and

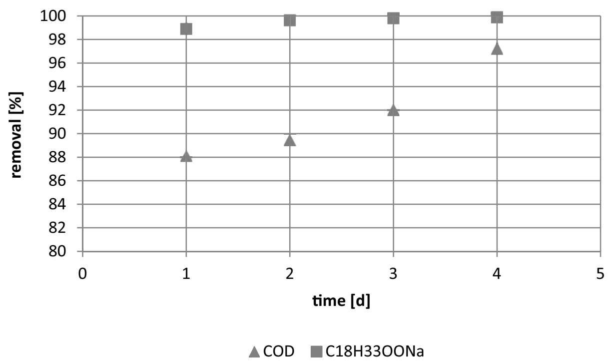

Fig. 2. Comparison of COD removal and sodium oleate removal during wastewater treatment in aerobic condition and F/M = 0.12 g COD g^{-1} d^{-1}.

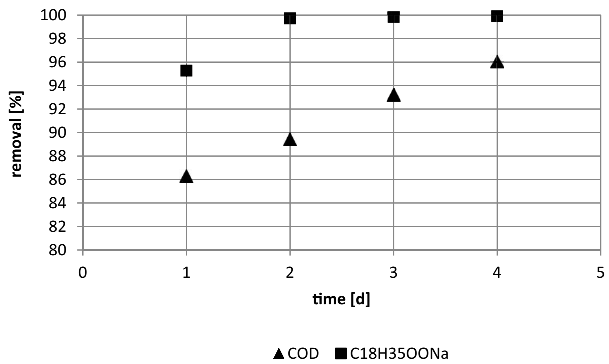

Fig. 3. Comparison of COD removal and sodium stearate removal during wastewater treatment in aerobic condition and F/M = 0.12 g COD g^{-1} d^{-1}.

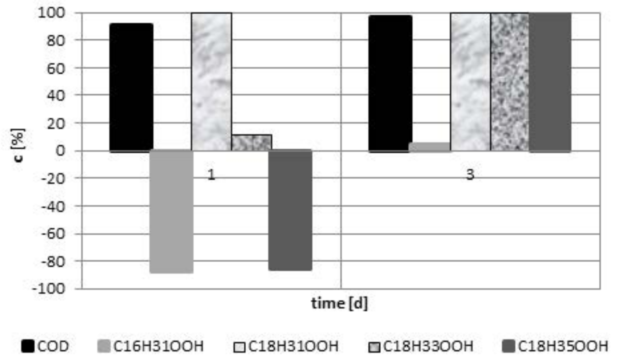

Fig. 4. Comparison of COD removal and four fatty acids removal during wastewater treatment in aerobic condition and F/M = 0.17 g COD g^{-1} d^{-1}.

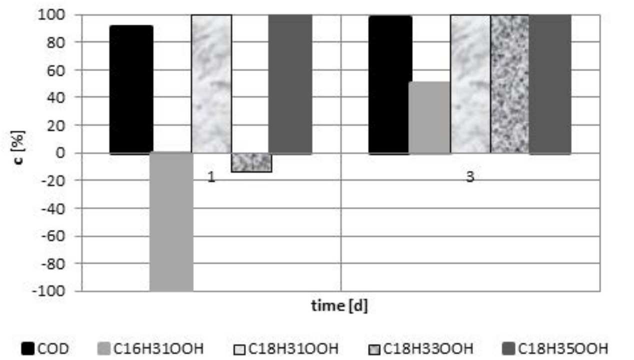

Fig. 5. Comparison of COD removal and four fatty acids removal during wastewater treatment in aerobic condition and F/M = 0.21 g COD g^{-1} d^{-1}.

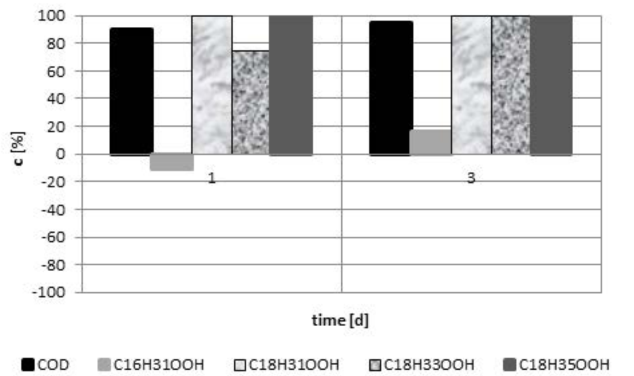

Fig. 6. Comparison of COD removal and four fatty acids removal during wastewater treatment in aerobic condition and F/M = 0.3 g COD g^{-1} d^{-1}.

substrates for biological reactions appeared. Unsaturated acid – linoleic acid ($C_{18}H_{31}OOH$) was 100% biodegraded. With the use of F/M ratio from 0.17 to 0.30 g COD g^{-1} d^{-1} unsaturated acid – oleic ($C_{18}H_{33}OOH$), and saturated acid – stearic acid ($C_{18}H_{35}OOH$) were also the fastest biodegradable (Figs. 4–6). It was different in the case of palmitic acid ($C_{16}H_{31}OOH$).

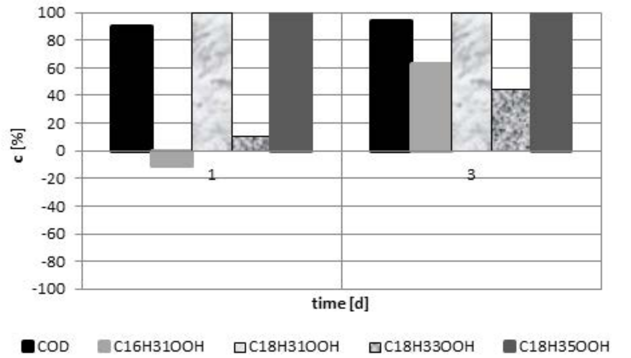

Fig. 7. Comparison of COD removal and four fatty acids removal during wastewater treatment in aerobic condition and F/M = 0.65 g COD g^{-1} d^{-1}.

For this acid, on the first day of the process, higher concentrations were observed (increase 10.5%–100%), and on the third day, also lower concentration (decrease 4.2%–63.2%) than the initial value. During biodegradation, caprylic acid ($C_8H_{15}OOH$), capric acid ($C_{10}H_{19}OOH$), and palmitoleic acid ($C_{16}H_{29}OOH$) also appeared in the wastewater as decomposition byproducts.

The rate of oil and fats biodegradation depends on the type of pollution, that is, vegetable oil or animal fat [18], saturated acids or unsaturated acids [19], the number of carbon atoms in chain [20]. Similar phenomena were found using bio-additive (*Pseudomonas fluorescens, Pseudomonas putida, Bacillus subtilis, Bacillus licheniformis*, and *Bacillus thuringiensis*) [19]. The unsaturated fractions are diminished while the saturated fractions increased as a result of degradation of the unsaturated fatty acids, and hydrogenation to the unsaturated form. Myristic acid ($C_{14}H_{27}OOH$) is more readily biodegradable than palmitic acid ($C_{16}H_{31}OOH$) [20]. Linoleic acid ($C_{18}H_{31}OOH$) and oleic acid ($C_{18}H_{33}OOH$) are more susceptible to oxidation [21].

Based on this study and the literature data, the following sequence of removal of fatty acids from wastewater can be found:

$$C_{18}H_{31}OOH > C_{18}H_{33}OOH > C_{18}H_{35}OOH > C_{16}H_{31}OOH$$

Under anaerobic condition, the accumulation of palmitic acid in sludge was observed because the transformation of oleic acid to palmitic acid was a fast and nonlimiting step in oleic acid degradation, while further degradation of palmitic acid was a difficult step [22].

In the sewage systems, fatty acids transformations may also take place via biological processes. Higher ratio of oleic acid to palmitic acid at the pumping station and lower at the inlet to the WTP were found [2].

During the biological wastewater treatment, the relationship between the appearance of FFA and their removal and technological parameter – substrate loading, was found. But there are many other technological parameters such as process temperature and oxygenation conditions and technological solutions of bioreactors, which may have the influence on the contaminants removal efficiency. The recognition of refractory compounds defines the selection of the optimal treatment technology (Figs. 2–7). Such a solution may be

MBRs for which a higher efficiency of wastewater treatment has been found [23]. Moreover, products of biodegradation of fatty acid salts and FFAs themselves can be retained on the membrane.

Currently, many studies concern the use of anaerobic membrane bioreactor (AnMBR) in domestic wastewater treatment [24–27]. AnMBR requires longer time to reach stable operation compared with aerobic MBR and organic removal is lower than that in aerobic MBR [24]. However, the use of innovative modifications will enable anaerobic domestic wastewater treatment at the same level – similar quality effluents – as aerobic treatment, while anaerobic treatment concurrently recovers useful energy and produces considerably less residuals [25,26]. HRT is comparable with conventional aerobic processes under ambient temperatures [26]. In the case of domestic wastewater, the membrane materials can also be important [27,28].

4. Conclusions

In this study, sodium salts of fatty acids and edible oil were used as exemplary substrates. The following conclusions were obtained:

- Sodium acetate (CH_3OONa) as a single substrate and wastewater (rapeseed oil emulsion at doses of 0.03% and synthetic wastewater) were biodegradable in a similar efficiency.
- Lower initial efficiency of the process was observed for sodium oleate ($C_{18}H_{33}OONa$) and sodium stearate ($C_{18}H_{35}OONa$) as a single substrate. It enabled to summarize that salts of unsaturated acids were biodegraded faster than saturated ones. Products of biodegradation still remained in treated wastewater as refractive compounds. Removal of COD was found at 89.5% and 89.4%.
- In the case of wastewater, COD removal was obtained at a similar level: 91.2%–89.6%, but fatty acids were removed to various efficiencies. Unsaturated acids – linoleic acid was 100% biodegraded (1d), oleic acid, and saturated acid – stearic acid was also 100% biodegraded (3d). However, palmitic acid appeared as a result of wastewater treatment.

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