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ESTIMATION OF BIODEGRADABILITY RATE OF POLLUTANTS IN SEWAGE FROM SELECTED SECTIONS OF DAIRY

The rate of biological degradation of effluents from some selected departments of a dairy was measured. The analyses were carried out for the wastewater from a milk pasteurization section, a butter factory, a cheese dairy, a wastewater pumping station (a mixture of sewage from the entire plant), as well as for sweet whey generated during production of hard cheeses. The examinations were carried out by the respirometric method using aerobic activated sludge. The content of organic matter oxidized over 5-day examinations was determined as converted into 1 g of activated sludge biomass. Analyses were carried out at the temperatures of 20 °C and 35 °C at a loading rate of the activated sludge A of 0.2 g COD/g TSS · d which enabled a total biological degradation.

The results testified to the relationship between a technological process responsible for the production of the sewage analysed, and dairy sewage biodegradability. The results confirmed that all dairy effluents can be treated together, with the exception of whey, whose complex biodegradation may cause too heavy burden to any wastewater treatment technological system and thus should be managed within a separate installation.

1. INTRODUCTION

Dairy sewage differs widely both in quantity and quality, depending on a given dairy production characteristics (RICO et al. [14]). Many products in dairies are manufactured separately, thus pollutant content in the dairy sewage at a given time changes, depending on a technological cycle of processing line. Such a correlation reduces the efficiency of sewage treatment in dairies. The problem might be particularly discernible in smaller dairies where it is fairly difficult to average and balance the sewage content. In 1995 and 1996, DANALEWICH et al. [3] carried out a research in some US dairies whose assortment and production scale were analo-

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gous. The researchers revealed that the effluent flow differed within a range of 170 and 2081 m^3/d. In most factories, the sewage flow volumetric intensity was observed to vary on a seasonal, diurnal and hourly bases, with the minimum effluent flow ranging from 4 to 170 m^3/d and the maximum from 257 to 2650 m^3/d. Diurnal and hourly fluctuations in the amount of sewage produced were connected with washing the appliances and rooms at the end of each processing cycle. Whereas seasonal lability was attributed to milk processing rates being higher in summer and lower in winter.

The organic compounds loading rate in dairy sewage is determined by the amount of lactose, fats and proteins (ŐZTURKET et al. [11], PERLE et al. [12]). The relationship between these substances can be extremely varied, which affects their susceptibility to biological treatment. Sewage reaction and temperature are other factors which determine biodegradation efficiency (ERGURDER et al. [4]).

Under anaerobic conditions ammonia and amino acids are the primary products of protein biodegradation. Some milk proteins, for instance casein, are resistant to biodegradation, therefore in order to be biodegraded they require microorganisms that are appropriately adapted. Some experiments show that biogas production from casein in the case of unadapted sludge (3.7 g COD/dm^3 d) achieves low values (0.25 cm^3 CH_4/h) with a lag phase of 50 h, whereas at the adapted sludge – 0.79 CH_4/h. Casein does not inhibit anaerobic changes within the concentration range of 0–3 g/dm^3 (PERLE et al. [12]).

In comparison to proteins, hydrocarbons are more susceptible to biodegradation which occurs easier and faster. Lactose, which is found in dairy sewage, is biodegraded to propionic acid, ethanol and acetate. Yet, the presence of some intermediate products of biodegradation, undissociated forms in particular, may hinder anaerobic changes (AGUILAR et al. [1]).

Biodegradation of fats may be rendered difficult as their biodegradability rate is very low (PETRUY and LETTINGA [13]). In dairy sewage, fats generate glycerol and long-chain fatty acids. Glycerol does not cause inhibition, whereas long-chain fatty acids, both saturated (12–14 carbon atoms) and unsaturated (18 carbon atoms) (PERLE et al. [12]), may be harmful to various microorganisms, to methanogenous bacteria in particular. Such a harmful effect is attributed to double bonds and *cis* isomers, which occur in natural fats.

The rate of biochemical decomposition of waste depends on the activity of microorganisms (precisely – on the enzymatic reaction rate). The activity of enzymes, and consequently the biochemical reaction rate, depends on the ambient conditions, i.e., the substrate concentrations, temperature, redox potential, osmotic pressure and on the presence of enzyme-activating and inhibiting substances.

The relationship between a reaction rate and temperature is expressed by the Van't Hoff–Arrhenius' equation. A transformed form of the equation is commonly used, which compares the reaction rates at different temperatures:

$$k_{T_1} = k_{T_2} \mathrm{e}^{\left[\left(\frac{E}{RT_1T_2}\right)(T_1 - T_2)\right]}, \tag{1}$$

where:

k_{T1} – the reaction rate constant at the temperature T_1 in variable units, depending on the reaction order,

k_{T2} – the reaction rate constant at the temperature T_2 in variable units, depending on the reaction order,

E – activation energy [J/mol],

R – universal gas constant [8.314 J/mol·K],

$T_{1,2}$ – the temperature [K].

A transformed form of the equation is more commonly applied in modelling the processes of waste treatment:

$$k_{T_1} = k_{20}\theta^{(T_1 - T_{20})}, \tag{2}$$

where θ is the temperature coefficient.

The effect of temperature on the enzyme-catalysed reaction rate is produced by two processes. An increase in temperature is accompanied by an enzyme-catalysed reaction, which is consistent with the Van't Hoff–Arrhenius' equation. However, because of the protein character of enzymes the relationship is only valid below a certain temperature value. An increase in temperature above the optimum value for a given enzyme brings about its denaturation.

Most bacteria which take part in waste treatment processes are mesophilic organisms (HENZE et al. [5]). It is assumed that the process rate in aerobic, heterotrophic decomposition of organic compounds increases exponentially according to equation (2) when temperature changes from 0 °C to 32 °C. Between 32 °C and 40 °C, the process rate is constant and afterwards it plummets to reach zero at 45 °C. The process of aerobic decomposition of organic compounds can run in thermophilic conditions between 50 °C and 60 °C. Under these conditions, the process rate will be by 50% higher than at 35 °C. The nitrification process rate increases with temperature until about 30–35 °C. When the temperature reaches 40 °C, the process rate drops to zero. No activity of nitrifying bacteria was found in thermophilic intervals of 50–60 °C. The relationship between the nitrification process and the temperature is similar to that observed during the aerobic decomposition of organic compounds. The process rate rises exponentially up to about 32–35 °C. It is assumed that the nitrification process can run at temperatures which are typical of thermophilic bacteria.

2. METHODOLOGY

2.1. THE SEWAGE CHARACTERISTICS

The research on the biodegradability of some dairy sewage was based on respirometric methods. In the experiment, the researchers used activated sludge adapted to dairy sewage biodegradation under aerobic conditions.

Table 1

Physical and chemical characteristics of the dairy sewage being analysed

The sewage origin	BOD_5 mg /dm^3	COD mg /dm^3	BOD_5/COD mg /dm^3	Total suspended solids mg /dm^3	Fats mg /dm^3	pH
Apparatus room	3470	14639	0.27	3821	3105	10.37
Butter section	2423	8925	0.27	5066	2882	12.08
Pumping station	797	2542	0.31	653	1056	7.18
Cheese section	3456	11753	0.29	939	330	7.90
Cottage cheese section	2599	17645	0.15	3375	950	7.83
Hard cheese whey	29480	73445	0.4	7152	994	5.80

The sewage selected for the experiment displayed diverse values of physical and chemical properties (table 1). It was collected from the following sections of the dairy processing line:

- The apparatus room – the sewage originated from washing the equipment such as centrifuges, devices and installations used for milk thermal processing, homogenisation, condensation and out-gassing (de-aeration). The sewage varied in content, depending on the detergents used for washing.
- The butter section – the sewage originated from washing the rooms, devices and installations used in butter production. Its characteristic feature was high content of fats.
- The milk reception point – the sewage originated from washing the cisterns, pipes, floors and drives. Its texture resembled highly-diluted milk.
- The cheese and cottage cheese section – the sewage originated from washing the devices and installations for hard cheese and cottage cheese production, respectively. It was marked by high rates of organic pollutants.

Apart from these the following liquids were analysed in the research:

- Hard cheese whey – a secondary product of hard cheese production (sweet whey).
- Cottage cheese whey – a secondary product of white cottage cheese production (sour whey).
- Mixed sewage – all the sewage combined in one stream (the pumping station sewage).

2.2. THE MEASUREMENT EQUIPMENT

The dairy sewage biodegradability rate under aerobic conditions was measured by means of respirometric Oxi-Top apparatus by WTW company. The measurement equipment consisted of a reaction tank and a recorder.

The reaction tank held an appropriate amount of the sewage analysed and a portion of activated sludge standardised for all measurements. The reaction tank was firmly attached to the recorder, which traced and registered the changes of partial pressure inside the reaction tank. For cellular respiration the microorganisms in the activated sludge used organic compounds from the sewage analysed. The measurements were carried out under aerobic conditions. The microorganisms used the oxygen from the reaction tank as the electrons' acceptor and in turn released carbon dioxide being an ultimate product of carbon compound changes under aerobic conditions. In the reaction tank, carbon dioxide was bound by the absorbent, sodium alkali (NaOH), which led to the change in the partial pressure inside the reaction tank. The pressure was automatically measured and registered by the recorder, which simultaneously converted the values of the registered partial pressure into the amount of oxygen used by the microorganisms.

Consistently, a single reaction tank was supplied with the same amount of the activated sludge biomass. Following that an appropriate amount of the dairy sewage was supplied, prior to which the content of organic compounds (COD) in the sewage had been defined. The experiment was conducted on the activated sludge at the applied pollutant loading COD of $A' = 0.2$ g COD/g TSS · d; the tests were carried out at the temperature of 20 °C and 35 °C. The measurement session lasted 5 days, during which 1.0 g of organic matter (COD) from the treated sewage per 1.0 g of the activated sludge dry mass was supplied at a time to the reaction tank. The activated sludge used in the research was obtained from the ancillary reactor operating in a time cycle (SBR). The sludge load in that reactor was maintained at the level of $A' = 0.2$ g COD/g TSS · d. The activated sludge used in the experiment was adapted to dairy sewage biodegradation. The culture medium used in the ancillary reactor comprised synthetic sewage which had been formed on the basis of powdered milk.

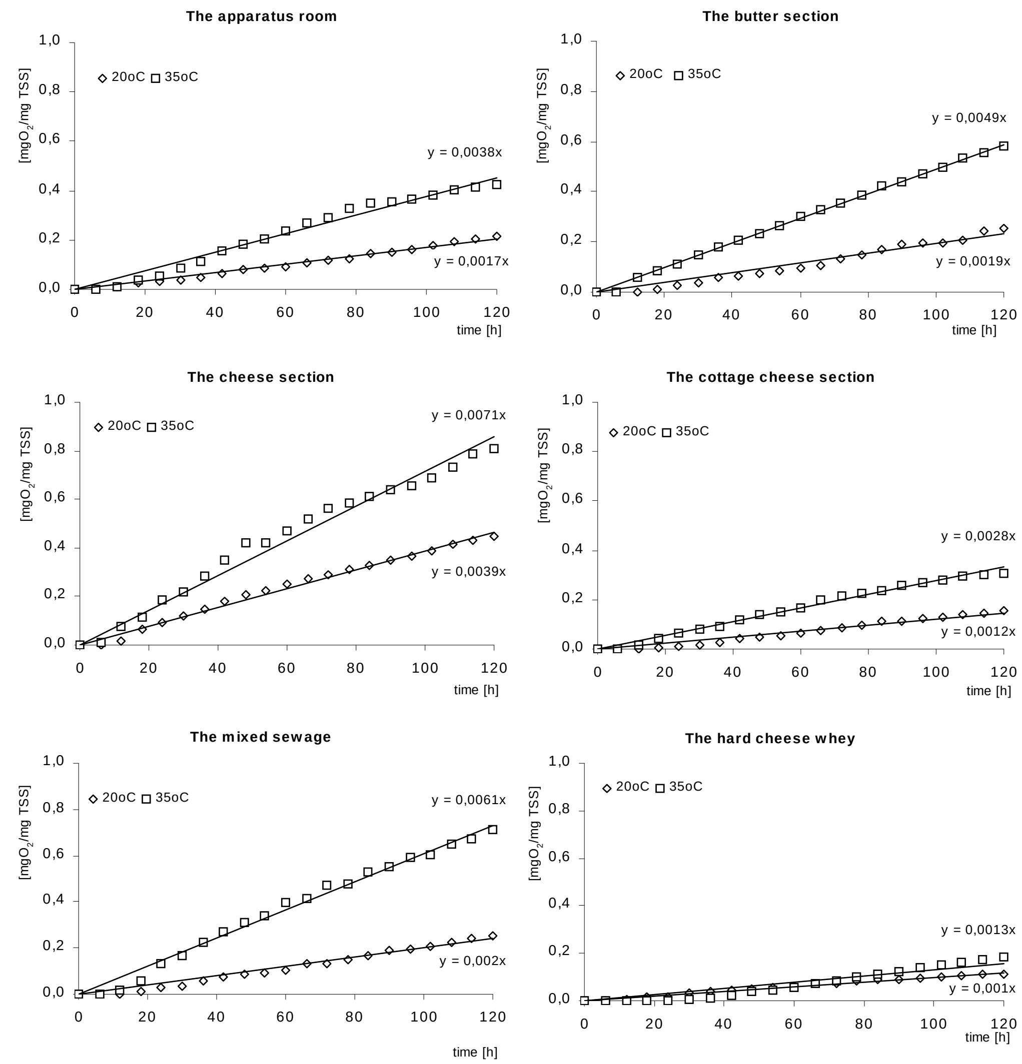
2.3. STATISTIC METHODS

In each temperature variant, the measurements were made in five replications irrespective of the type of the wastewater examined. The results obtained were processed to determine the mean value, standard deviation and standard error of the mean. If the value of standard error was below 10%, it was assumed that the results were characterized by a low variability, and the mean value calculated was reliable. Thus, the mean values obtained were used to determine the final results that were calculated as a mean value of results recorded for particular sample collections. They, in turn, were used to estimate the constants of the reaction rate. The constants were determined based on experimental data using the non-linear regression method. A conformity index φ^2 was accepted as a measure of curve matching to experimental data, which enabled the reaction order and reaction rate constant k to be determined.

3. RESULTS

The susceptibility of dairy wastewaters was subject to changes, depending on the production process they originated from. The processing methods of raw material determine the quality and composition of wastewaters produced, which in turn affects decomposition rate of effluents occurring in sewage. In all the types of sewage under examination, the decomposition process of organic compounds proceeded according to the zero-order reaction, irrespective of the fact whether the measurements were carried out at a temperature of 20 °C or 35 °C.

The highest rate of oxidation was observed in the case of wastewaters originated from the cheese dairy. At a temperature of 20 °C, the decomposition rate r reached 0.0039 mg O_2/mg TSS · h. The elevation of the process temperature to 35 °C increased the reaction rate up to 0.0071 mg O_2/mg TSS · h (figure). At a temperature of 20 °C, the decomposition rates of sewage from the pumping station and butter factory were similar and accounted for r = 0.0020 mg O_2/mg TSS · h. Also, in the case of wastewater from the butter factory, the oxidation of organic compounds was observed to proceed at a negligibly lower rate, i.e., r = 0.0017 mg O_2/mg TSS · h. A rise in the process temperature to 35 °C resulted in a twofold increase in the decomposition rate of wastewaters from the butter factory and the milk pasteurization section. At a higher temperature, sewage from the pumping station, being a mixture of effluents from all production lines, was observed to decompose at over threefold higher rate, i.e., r = 0.0061 mg O_2/mg TSS · h (figure). Of all the six departments of dairy production examined, the least decomposable appeared to be the wastewaters from fresh white cheese dairy and whey originating from the production of hard cheeses. The decomposition rate of sewage from fresh white cheese dairy accounted for r = 0.0012 mg O_2/mg TSS · h at a temperature of 20 °C and for r = 0.0028 mg O_2/mg TSS · h at a temperature of 35 °C. The oxidation of whey appeared to proceed at the lowest rate at both temperature intervals. Moreover, in the case of those effluents, a rise in temperature accelerated the oxidation process only to a slight extent. At a temperature of 20 °C, the decomposition rate r reached 0.0010 mg O_2/mg TSS · h, whereas at 35 °C the oxidation rate was as low as 0.0013 mg O_2/mg TSS · h (figure).



Decomposition rate of wastewaters from selected dairy production departments

The determined values of a temperature coefficient θ indicate a correlation between the oxidation rate of effluents and the temperature of the process. Of the wastewaters examined, an increase in temperature affected to the greatest extent the decomposition of effluents contained in the sewage from the pumping station. The value of the temperature coefficient accounted for $\theta = 1.077$ (table 2). Also, in the case of sewage from the butter factory, the rate of the oxidation process was observed to increase considerably with a temperature rise to 35 °C. The temperature coefficient θ reaching 1.065 testified to an over two times higher amount of oxidized organic matter when converted into dry matter of the activated sludge used in the study (table 2). The elevated temperature was observed to have the least significant effect on the decomposition rate of whey, for which the temperature coefficient θ was the lowest and reached 1.012. A rise in temperature practically did not increase the amount of the oxidized organic matter.

Table 2

Values of temperature coefficient θ

Waste source	Temperature coefficient θ
Apparatus room	1.056
Butter section	1.065
Cheese section	1.041
Cottage cheese section	1.042
Mixed sewage	1.077
Hard cheese whey	1.012

4. DISCUSSION

Major components of dairy effluent are as follows: a high load of organic compounds, some lipids, suspension and biogenic elements. In the case of dairy sewage, the proportions of lipids, proteins and carbohydrates may be very differentiated, which is of significant importance to the possibilities of their treatment (ERGURDER et al. [4]).

In general, carbohydrates are more readily and rapidly decomposed compared to proteins. Lactose present in dairy sewage decomposes to propionic acid, ethanol and acetate. Nevertheless, the presence of intermediate forms of decomposition, especially of the non-dissociated ones, is likely to inhibit biological transformations (AGUILAR [1]). The biodegradation of lipids is hindered due to their low biosusceptibility to decomposition (PETRUY and LETTINGA [13]). Lipids in the dairy sludge are degraded to glycerol and long-chain fatty acids. Glycerol has been reported not to exert an inhibiting effect (PERLE et al. [12]), whereas the long-chain saturated (12–14 C) and unsaturated (18 C) fatty acids have been reported to be detrimental to various microorganisms, especially to methanogenic bacteria. Their harmful effect is linked with double bonds and *cis* isomers present in natural lipids.

The presence of lipids caused that sewage from the butter factory was decomposed at a slower rate than the wastewaters from cheese dairy oxidized at the highest rate. A rise in the process temperature to 35 °C resulted in a remarkably increased decomposition rate of sewage from the butter factory. This was linked with easier emulsification of lipids at a higher temperature, thus with their increased susceptibility to hydrolyzing enzymes. The high decomposition rate of sewage from the cheesemaking process testifies to a high content of carbohydrates. Contrary to expectations, the decomposition process of wastewaters from the milk pasteurization section did not indicate any negative influence on chemical agents used for rinsing and washing the system. The washing process of a dairy system involves a number of detergents and disinfecting agents (DANALEWICH et al. [3]). These substances reveal, most of all, antiseptic and bactericidal activities as well as a contribution to an increased load of organic effluents in sewage by reducing the BOD_5/COD ratio and to increased concentration of biogenic elements. As demonstrated in the study, the decomposition rate of sewage from the milk pasteurization section was comparable and even higher than that of effluents originating from the other sources. In aerobic decomposition of sewage from the milk pasteurization section, no lag phase occurred. The oxidation of effluents was observed immediately after the measurement had commenced. A high decomposition rate of effluents in the sewage originating from the pumping station is highly interesting. This sewage was a mixture of effluents from all the sources analyzed. Its high decomposition rate r of 0.0061 mg O_2/mg TSS · h was most likely due to the fact that it was subject to putrefaction in a storage reservoir, which resulted in the production of readily available volatile acids. In contrast, wastewaters from the other sources were subjected to analyses immediately when produced.

Of all effluents examined, definitely the lowest oxidation rate was observed for those of whey originating from the production of hard cheeses. Cheese whey, a product of the cheesemaking industry, is rich in proteins and lactose. As much as 99 % of whey is biodegradable and its high content of organic matter being referred to as chemical oxygen demand (COD) – reaching 70 g COD/dm^3 on average. Yet, compared to this high load, it demonstrates low alkalinity, i.e., 2500 mg $CaCO_3$/dm^3 (MAWSON [9]). For this reason, the oxidation of whey may be rendered difficult. MALASPINA et al. [8] reported that whey may be troublesome during anaerobic treatment due to its low alkalinity, which leads to rapid souring. Moreover, whey poses problems with the production of pelleted sludge as well as tends to produce excessive amounts of viscous exopolymers, most probably of bacterial origin inhibiting the floccules' capacity for sedimentation which, in turn, may cause their washing out (VIDAL et al. [15]). Problems with the utilization of whey were confirmed in the study reported. Even at a temperature of 35 °C the decomposition rate of whey was over twice as low as that of second-in-row effluents from fresh white cheese dairy and over five times lower than that of effluents from the cheese dairy decomposed at the highest rate.

Investigations into the decomposition of effluents originating in different stages of dairy production were carried out at two temperatures: 20 °C and 35 °C. According to the Van't Hoff–Arrhenius equation, the reaction rate increased along with a rise in the process temperature. In this equation, the reaction rate at a specified temperature is referred to the reaction rate at a standard temperature of 20 °C. The temperature coefficient θ, present in the equation, enables determining to what extent the changes in temperature affect the reaction rate. However, it is emphasized that the equation is true for the systems in which the rate is not limited by a substrate concentration

(LEWANDOWSKI [7]). The values of the temperature coefficient θ allowed the correlation between the culture medium (type of sewage) applied and the effect of temperature on the activity of the sludge to be analyzed. An increase in the process temperature was found to have the weakest impact on the decomposition rate of effluents from whey, and the most profound effect on the decomposition of sewage originating from the intermediate pumping station. HENZE et al. [5] suggest that a low value of the temperature coefficient (θ = 1.07) is typical of heterotrophic processes. KADLEC and REDDY [6] claim that temperature has a negligible impact on BOD_5 removal. During the aerobic decomposition of organic matter, the value of the temperature coefficient θ reached 1.08 for activated sludge and 1.035 for biological filters. The coefficient values reported by these authors confirmed the lower susceptibility of biological filters to unfavourable changes in temperature determined by other authors (ANDERSSON [2]) compared to that of the activated sludge. The studies by MAYO and NOIKE [10] into heterotrophic bacteria cells' capability to form colonies have demonstrated no differences in the process rate at temperatures of 20 °C and 35 °C. In addition, these authors have emphasized that, under stable conditions, the heterotrophic bacteria were not susceptible to temperature changes within the range of 10–20 °C. The numbers of these bacteria at temperatures of 10 and 20 °C were similar. WU et al. [16] demonstrated that at temperature over 15 °C an increase in the removal efficiency of organic compounds was directly proportional to the increasing temperature, and that above 25 °C the efficiency declined. KADLEC and REDDY [6] claimed that the reaction of microorganisms was determined by temperature to a greater extent at its lower range, i.e., <15 °C, compared to its optimal range of 20–35 °C, and that temperature changes within the latter range had a negligible impact on BOD_5 removal.

The research demonstrated that in the case of dairy wastewaters, a rise in temperature (from 20 to 35 °C) affected greatly the decomposition rate of effluents. Taking into account the reports on the lack of a significant effect of thermal conditions on the activity of heterotrophic bacteria in the temperature range of 20–35 °C, it may be assumed that a rise in process temperature contributes mainly to the improvement of substrate availability (more readily decomposable forms), through, e.g., more efficient emulsification of lipids or more rapid production of volatile acids. This has been confirmed by high values of the temperature coefficients θ in the case of sewage from the butter factory and pumping station.

The determined values of the decomposition rate of effluents clearly indicate that it is advisable to carry out the process of dairy sewage treatment at higher temperatures. It would be tantamount to the possibility of applying reactors with lower volumes. Moreover, in the dairy industry, it does not entail the need for providing an external source of heat to the reactor, as in most cases the temperature of wastewaters discharged from the production plants is definitely over 25 °C. It would be just enough to assume an appropriate thermal insulation in the technical design of a reactor.

5. CONCLUSIONS

1. The decomposition rate of dairy sewage was linked with its origin, which had a direct impact on the content and quality of proteins, lipids and carbohydrates occurring in wastewaters.

2. A rise in the process temperature from 20 °C to 35 °C caused a considerable increase in the decomposition rate of effluents originated from the sewage examined. The only exception were the effluents contained in whey.

3. A higher decomposition rate of the effluents at a temperature of 35 °C was more likely to result from the presence of more readily decomposable forms of effluents (e.g., upon lipid emulsification) than from the increased activity of bacteria.

4. No inhibitory effect of chemical agents was observed on the decomposition of sewage originated from the milk pasteurization section.

5. The high decomposition rate of effluents from the pumping station resulted from their initial anaerobic decomposition in the fermentation process proceeding in the storage reservoir. Thus, the increased concentration of volatile fatty acids contributed to a more rapid decomposition of the effluents under aerobic conditions.

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OSZACOWANIE SZYBKOŚCI BIOLOGICZNEGO ROZKŁADU ZANIECZYSZCZEŃ W ŚCIEKACH POCHODZĄCYCH Z WYBRANYCH DZIAŁÓW MLECZARNI

Przedstawiono wyniki pomiarów szybkości biologicznego rozkładu zanieczyszczeń znajdujących się w ściekach powstałych w wybranych działach mleczarni. Badano ścieki pochodzące z aparatowni, masłowni, serowni, pompowni ścieków (mieszanina ścieków z całego zakładu) oraz serwatkę słodką powstającą podczas produkcji serów twardych. Badania przeprowadzono metodą respirometryczną, wykorzystując tlenowy osad czynny. Określono ilość materii organicznej utlenionej podczas pięciodniowego pomiaru w przeliczeniu na jeden gram biomasy osadu czynnego. Badania przeprowadzono w temperaturze 20 °C i 35 °C przy obciążeniu osadu czynnego 0,2 g BZT/g s.m.·d zapewniającym całkowity rozkład biologiczny.

Wyniki badań wykazały zależność między procesem technologicznym, w wyniku którego powstawały badane ścieki, a możliwością ich biologicznego rozkładu. Stwierdzono, że wszystkie strumienie zanieczyszczeń powstających w mleczarni mogą być oczyszczane razem. Wyjątkiem jest serwatka, która ze względu na utrudniony biologiczny rozkład stanowi istotne obciążenie każdego układu technologicznego oczyszczania ścieków i powinna być zagospodarowywana w oddzielnej instalacji.