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COD fractions changes in the SBR-type reactor treating municipal wastewater with controlled percentage of dairy sewage

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Abstract. The aim of study was to investigate the influence of percentage of dairy wastewater in the municipal wastewater on the changes of COD fractions during the cycle of SBR-type reactor. The scope of the research included physicochemical analyses of municipal wastewater without dairy wastewater, dairy wastewater, mixture of municipal and dairy wastewater as well as treated sewage. Both the concentrations and the proportions between COD fractions changed in the SBR cycle. In raw municipal and dairy wastewater - X_S, insoluble hardly bio-degradable fraction of COD dominated (49.6 and 64.5% respectively). In treated wastewater S_I, COD for dissolved compounds that are not biologically decomposed (inert) (from 62.1 to 74.6%) dominated, while X_S fraction was from 19.1 to 24.4%. The consumption rate of organic compounds depended on the type of COD fraction, SBR cycle phase and the percentage of dairy wastewater. The highest rates of organic compounds consumption were noted in the phase of mixing. In the case of fraction S_I, no differences in concentration in the SBR cycle time, were found. Concentration of COD in treated wastewater was from 34.8 to 58.9 $mgO_2 \cdot L^{-1}$ (efficiency wastewater treatment from 96.0 to 98.6%).

1 Introduction

The dairy industry is one of the biggest sources of industrial wastewater in Europe [1-2]. It generates wastewater characterized by a high content of organic compounds expressed as biochemical oxygen demand (BOD) or chemical oxygen demand (COD). The biodegradability of wastewater depends, among other things, on the availability of organic compounds (in the forms of dissolved compounds or suspensions) for microorganisms, substrate type, adaptation of the system, presence of toxic compounds, and temperature [3-4]. The most frequently used parameters characterizing the biodegradability of wastewater include the COD/BOD_5 ratio. Its value above 2.5 indicates a high share of hardly biodegradable or non-biodegradable impurities, while a value below 1.8 indicates the

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susceptibility of wastewater to biological decomposition [5]. However, in many cases this information is insufficient.

Dairy wastewater treatment uses membranes, coagulation, flotation and electrochemical, methods. In the case of biological treatment, anaerobic and aerobic methods are commonly used, as well as co-treatment of dairy and municipal wastewater, which most frequently operate using activated sludge technology. This results from the fact that dairy wastewater is characterized by a C:N:P ratio suitable for supporting denitrification and biological dephosphatation, and is source of so-called volatile fatty acids (VFA) in the process line [1, 6-9].

For understanding the processes of decomposition of organic compounds and purification of wastewater, COD fractioning is helpful [10]. It allows for a detailed characterization of the composition of wastewater in regard of their biodegradability, as well as changes in the individual fractions during the specific technological processes. This information is necessary for modelling the operation of a wastewater treatment plant.

Four COD fractions are distinguished in municipal wastewater: a fraction of dissolved easily biodegradable compounds – S_S; a fraction of dissolved compounds which are not biologically decomposed (inert) – S_I; a fraction of insoluble hardly biodegradable compounds – X_S, and a fraction of undissolved compounds which are non-biodegradable (inert) – X_I.

The goal of the research was to determine changes in the values and relationships between the individual COD fractions during the treatment of municipal wastewater with a controlled share of dairy wastewater in laboratory reactors of the SBR type.

2 Methods

The tests were carried out using 8 reactors of the SBR type (R1-R8), to which the municipal wastewater (MW) and the dairy wastewater (DW) were supplied. The activated sludge used in the studies was collected from an SBR type reactor in Hajnówka (Poland), treating municipal wastewater which contain a 10% share of dairy wastewater. The average volume of milk processed in the plant, from which the DW was collected, amounted to 160 $m^3 \cdot day^{-1}$.The water consumption index per the amount of the milk processed was 3.36 $m^3 \cdot m^{-3}$. In dairy plant, wastewater connected with the production of ripening cheeses, creamed cheeses of Swiss type, butter, cottage cheeses, powdered milk, and cream, is generated.

The wastewater supplied to the individual laboratory reactors of the SBR type differed in the MW and DW percentages (R1 – 100% MW, 0% DW; R2 – 95% MW, 5% DW; R3 – 90% MW, 10% DW; R4 – 85% MW, 15% DW; R5 – 80% MW, 20% DW; R6 – 70% MW, 30% DW; R7 – 50% MW, 50% DW; R8 – 0% MW, 100% DW). The volume of the MW-DW mixture was 5 L, whereas the volume of the activated sludge and the treated wastewater remaining in the reactor after a previous cycle - 8 L. The activated sludge concentration was maintained at the level of 3.7 $kg \cdot m^{-3}$.

For 72 hours (nine 8-hour cycles), the contents of reactors were subjected to technological regime, in which the sequence and duration of the purification process phases was the same as in the sewage treatment plant, from where sludge and municipal wastewater was collected (prior to its merging with dairy sewage stream). The SBR phases included: filling and mixing - 20 min., aeration and mixing - 300 min., sedimentation - 100 min., decanting - 60 min. Then relevant studies were conducted, which lasted another 3 days (9 cycles). Samples for analysis of physicochemical properties were collected in cycle 1, 4, and 9. The concentration of the dissolved oxygen, pH, and wastewater temperature were measured directly in the reactors (using a Hach HQd Meter and IntelliCAL Smartprobes, Germany) (Table 1). Determinations of COD, BOD_5 and total suspended solids were carried out according to the APHA [11]. The COD fractions were calculated according to methods described by Struk-Sokołowska [12].

3 Results and discussion

The classification of COD into easily biodegradable substance and hardly biodegradable or non-biodegradable substance in the dissolved form and in suspensions is commonly used in the modelling of wastewater treatment processes. According to the literature data, the share of the dissolved fraction in the total COD for domestic wastewater amounts to 21-35% on average, while that of the suspended fraction – 65-79%. Biodegradable organic compounds constitute on average 60-80% of all organic substances. The S_S and X_S fractions have the highest effect for biological wastewater treatment processes. Moreover, the S_S fraction may be used by the microorganisms directly, while the X_S requires a previous hydrolysis under the influence of extracellular enzymes, thanks to which these substances are transferred into the dissolved fraction. The COD value of the S_I and X_I fractions undergoes the smallest changes as a result of the activity of microorganisms. A part of the X_I fraction is removed together with the excess biomass [13-16].

Table 1. The values of pH, temperature and dissolved oxygen in raw wastewater and after the various phases of SBR.

Parameter	Sample	R1	R2	R3	R4	R5	R6	R7	R8
pH	A	7.0	6.9	6.9	6.9	6.8	6.8	6.7	6.5
	B	7.0	7.0	7.0	6.9	6.9	6.9	6.9	6.9
	C	7.0	7.0	7.0	7.0	7.0	6.9	6.9	7.0
	D	7.2	7.2	7.2	7.1	7.1	7.1	7.1	7.1
	E	7.2	7.1	7.1	7.1	7.1	7.1	7.1	7.1
	F	7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.1
	G	7.1	7.1	7.1	7.1	7.1	7.1	7.1	7.1
Temperature [^{0}C]	A	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
	B	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
	C	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
	D	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
	E	22.8	22.8	22.8	22.8	22.8	22.8	22.8	22.8
	F	22.9	22.8	22.8	22.9	22.8	22.9	22.9	23.0
	G	23.1	23.0	23.1	23.1	23.0	22.9	23.0	23.1
Oxygen concentration [$mgO_2 \cdot dm^{-3}$]	A	3.1	3.6	2.3	2.9	3.2	4.1	5.1	7.3
	B	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	C	0.1	0.0	0.1	0.0	0.1	0.1	0.1	0.1
	D	1.0	1.0	0.9	1.1	0.9	0.6	1.0	1.0
	E	3.1	3.0	3.2	3.2	3.0	3.2	3.1	3.3
	F	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.1
	G	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.0

A – raw wastewater. **B** – wastewater after filling SBR. **C** – wastewater after 20 min. mixing. **D** – wastewater after 150 min. aeration and mixing. **E** – wastewater after 300 min. aeration and mixing. **F** – wastewater after sedimentation. **G** – wastewater after decantation

In the tests carried out, the increase in the share of dairy wastewater was accompanied by an increase in the COD value in the raw wastewater; also, the ratios between the individual fractions changed. This resulted from the diversification of municipal and dairy wastewater (Table 2). In the municipal wastewater (R1, 100% MW), fractions undergoing biodegradation both in their dissolved form and as suspensions prevailed. The X_S fraction constituted 49.6% (449.2 $mgO_2 \cdot dm^{-3}$), while the S_s fraction amounted to 31.3%

(284.1 $mgO_2 \cdot dm^{-3}$). In the dairy wastewater (R8, 100% DW), undissolved fractions prevailed, both the biodegradable fraction and the inert fraction. The X_S fraction constituted 64.5%, and its value was six times higher than that of the municipal wastewater (2698.6 $mgO_2 \cdot dm^{-3}$). The X_I fraction constituted 21.5% (899.5 $mgO_2 \cdot dm^{-3}$) compared to 16.5% in the municipal wastewater, and its concentration was approximately six times lower (149.7 $mgO_2 \cdot dm^{-3}$). The S_S fraction constituted 13.2% in the dairy wastewater. However, its value was two times higher than that of the municipal wastewater (551.4 $mgO_2 \cdot dm^{-3}$). Both in the municipal wastewater and in the dairy wastewater, the lowest percentage was characterised by the S_I fraction, 2.6 and 0.9% (23.9 and 36.6 $mgO_2 \cdot dm^{-3}$), respectively.

The largest drop of the COD value in the treated wastewater occurred as a result of the dilution with sludge and the treated wastewater remaining in the reactor after a previous cycle, with the mixture. It amounted to 81.6% (R1) to 93.2% (R8). It corresponded to the values of the total COD from 166.5 $mgO_2 \cdot dm^{-3}$ (R1) to 285.8 $mgO_2 \cdot dm^{-3}$ (R8). The biodegradable fractions S_S and X_S prevailed. However, with a lower share of dairy wastewater, higher values were found for the dissolved fraction (R1-R3), while with a higher amount of dairy wastewater, higher values were found for the undissolved fraction (R4-R8).

The percentages of the individual COD fractions of municipal wastewater with various shares of dairy wastewater varied in comparison to other wastewater from the food industry. The studies performed by Chiavol *et al.* [17], the share of biodegradable fractions in wastewater from an olive oil press, subjected to treatment process in SBR reactors, amounted to 66.6% (S_S 29.2%; X_S 37.4%), while that of non-biodegradable fractions – 33.4% (S_I 9.9%; X_I 23.5%). Municipal wastewater with dairy wastewater had a higher share of X_S and lower shares of S_I and X_I. On the other hand, Rodriguez *et al.* [18] while analysing the composition of wastewater from the food industry, found that the shares of non-biodegradable fractions (inert) S_I and X_I in wastewater from the processing of tomatoes, sugar beet, potatoes, and from winemaking amounted to 18.4, 18.9, 28.8 and 20.9%, respectively.

In the phase of 20-minute mixing, organic compounds were consumed in denitrification and biological dephosphatation processes (Table 1-2) [19]. Depending on their availability (dissolved or suspended compounds), they were consumed at various rates. In this phase, a decrease in the value of the S_S fraction in reactors R1, R2, R3 and R5 was observed. The highest value (56.3 $mgO_2 \cdot dm^{-3}$) was found in R3, and the lowest one (41.6 $mgO_2 \cdot dm^{-3}$) – in R5. In R4 and R6, the S_S fraction value decreased slightly, but simultaneously its percentage in the total COD increased. In the reactors with significant shares of dairy wastewater (R7 – 50% of dairy wastewater; R8 – dairy wastewater only), an increase in the S_S fraction value was found, accompanied by an increase in its percentages. This was probably caused by the hydrolysis of organic compounds present in the composition of the X_S fraction, which prevailed in these reactors [14-15]. The compounds which were not consumed by microorganisms directly passed to the S_S fraction. As a consequence, the highest share of the S_S fraction (60.6%) in the wastewater after the 20-minute mixing phase was found in R8. Values and percentages of the X_S and X_I fractions in R3, R4, R6, R7 and R8 decreased, while in R2 their increase was found. In R1 and R5, the values of the X_S and X_I fractions decreased, while their percentage in the total COD increased. Values of S_I did not change in wastewater collected from each SBR. and their percentages increased.

In the results of 150-minute aeration and mixing of the SBR contents (the duration of the whole phase amounted to 300 minutes), a decrease in the value and percentage of the S_S fraction was found. R1 and R5 were exceptions; the value of the S_S fraction decreased there, although its percentage increased. Simultaneously, the largest decrease in the percentage of the X_I fraction was found in these reactors. The highest values of the S_S

fraction (42.7 $mgO_2 \cdot dm^{-3}$) were found in R4, while the lowest one (14.6 $mgO_2 \cdot dm^{-3}$) – in R2. In the case of the X_S and X_I fractions, decreases in the value and the percentage was found in six reactors. In R3 and R4, their values decreased, while their percentages increased. The S_I values did not change, and its percentages increased, which resulted from the use of organic compounds from other fractions.

Table 2. The mean values of COD fractions in raw wastewater and after the various phases of SBR.

SBR	COD fractions	A	B	C	D	E	F	G
		$mgO_2 \cdot dm^{-3}$						
R1	S_S	284.1	72.1	48.1	32.1	12.0	0.9	<0.1
	S_I	23.9	23.9	23.9	23.9	23.9	23.9	23.9
	X_S	449.2	52.9	43.6	16.2	4.7	9.1	8.3
	X_I	149.7	17.6	14.5	5.4	1.6	3.0	2.8
	Total COD	906.9	166.5	130.1	77.6	42.2	36.9	35.9
R2	S_S	327.6	124.6	43.6	14.6	7.4	1.8	<0.1
	S_I	24.4	24.4	24.4	24.4	24.4	24.4	24.4
	X_S	505.7	17.1	48.1	27.1	5.9	8.2	10.0
	X_I	168.6	5.7	16.0	9.0	2.0	2.7	3.3
	Total COD	1026.3	171.8	132.1	75.1	39.7	37.1	37.7
R3	S_S	300.3	76.3	56.3	16.3	7.2	5.2	<0.1
	S_I	23.7	23.7	23.7	23.7	23.7	23.7	23.7
	X_S	566.4	65.4	43.7	25.4	9.5	3.1	8.3
	X_I	188.8	21.8	14.6	8.5	3.2	1.0	2.8
	Total COD	1079.2	187.2	138.3	73.9	43.6	33.0	34.8
R4	S_S	284.7	60.7	58.7	42.7	2.7	0.9	<0.1
	S_I	26.3	26.3	26.3	26.3	26.3	26.3	26.3
	X_S	748.6	89.3	24.6	20.6	10.6	9.1	10.0
	X_I	249.5	29.8	8.2	6.9	3.5	3.0	3.3
	Total COD	1309.1	206.0	117.8	96.5	43.1	39.3	39.6
R5	S_S	289.6	84.6	41.6	25.6	6.4	0.9	<0.1
	S_I	24.4	24.4	24.4	24.4	24.4	24.4	24.4
	X_S	843.7	82.1	75.1	7.7	6.9	10.8	8.3
	X_I	281.2	27.4	25.0	2.6	2.3	3.6	2.8
	Total COD	1438.9	218.5	166.1	60.3	40.0	39.7	35.5
R6	S_S	278.9	52.9	51.9	13.9	2.5	0.2	<0.1
	S_I	26.1	26.1	26.1	26.1	26.1	26.1	26.1
	X_S	987.8	80.4	14.8	6.1	10.8	9.8	6.7
	X_I	329.3	26.8	4.9	2.0	3.6	3.3	2.2
	Total COD	1622.1	186.2	97.7	48.1	43.0	39.4	35.0
R7	S_S	385.9	60.9	76.9	28.9	3.1	2.2	<0.1
	S_I	30.1	30.1	30.1	30.1	30.1	30.1	30.1
	X_S	1180.8	105.8	39.8	4.4	20.2	6.1	8.3
	X_I	393.6	35.3	13.3	1.5	6.7	2.0	2.8
	Total COD	1990.4	232.1	160.1	64.9	60.1	40.4	41.2
R8	S_S	551.4	52.4	102.4	24.4	1.5	1.4	<0.1
	S_I	36.6	36.6	36.6	36.6	36.6	36.6	36.6
	X_S	2698.6	147.6	22.6	8.9	28.5	15.3	16.7
	X_I	899.5	49.2	7.5	3.0	9.5	5.1	5.6
	Total COD	4186.1	285.8	169.1	72.9	76.1	58.4	58.9

A – raw wastewater. **B** – wastewater after filling SBR. **C** – wastewater after 20 min. mixing. **D** – wastewater after 150 min. aeration and mixing. **E** – wastewater after 300 min. aeration and mixing. **F** – wastewater after sedimentation. **G** – wastewater after decantation

Further aeration and mixing (150 min) of the SBR content in all reactors led to a decrease in the values and percentages of the S_S fraction. The highest value (12.0 $mgO_2 \cdot dm^{-3}$) was found in R1 (100% MW), while the lowest one (1.5 $mgO_2 \cdot dm^{-3}$) –

in R8 (100% DW). In these reactors, the S_S fraction constituted 28.4 and 2.0%. respectively. The value of the S_I fraction did not change, similarly as in the earlier phases, while simultaneously its percentage in the total COD increased. The values of the X_S and X_I fractions in R1-R5 decreased, while in R6-R8, they increased. This probably resulted from an increase in the availability of organic substances in the form of suspensions (R1-R5), while in the reactors R6-R8 the total amount of organic compounds could be so high in relation to the demand of the microorganisms that a part of the energy was stored in synthesised extracellular polymeric compounds, thereby increasing the amount of the undissolved COD fractions [1, 14-15]. Depending on the changes in the other fractions, the percentages of X_S and X_I decreased (R1-R3) or increased (R4-R8).

In the sedimentation phase only a slight decrease in the value of the total COD in the treated wastewater occurred (below 1% in relation to the value after the aeration phase - except R7 and R8). Despite this, a further decrease in the percentages and the values of the S_S fraction in all reactors was found. The lowest value (0.2 $mgO_2 \cdot dm^{-3}$) was found in R6, the highest one (5.2 $mgO_2 \cdot dm^{-3}$) – in R3. The percentages of the S_S fraction constituted 0.5 and 15.8% of the total COD, respectively. Similarly as in the earlier phases, the S_I fraction did not change its value, and its percentage increased. In the case of the X_S and X_I fractions, an increase in their values and percentages in R1. R2 and R5 was found (in R1: X_S from 9.1 to 24.7%. X_I from 3.0 to 8.1%; in R2: X_S from 8.2 to 22.1%. X_I from 2.7 to 7.3%; in R5: X_S from 10.8 to 27.2%. X_I from 3.6 to 9.1%). In other reactors a decrease in the values and the percentages was found. The highest X_S value (15.3 $mgO_2 \cdot dm^{-3}$) was confirmed in R8, while the lowest one (3.1 $mgO_2 \cdot dm^{-3}$) – in R3. In the same reactors, the highest and the lowest value of the X_I fraction was ascertained (5.1 and 1.0 $mgO_2 \cdot dm^{-3}$, respectively). Similarly as the sedimentation phase, the decantation phase did not cause significant changes in the value of the total COD. Total efficiency of the removal of organic compounds was from 96.0% (R1) to 98.6% (R8). No presence of the S_S fraction was found in the treated wastewater, proving the use of easily biodegradable organic compounds irrespective of the dairy wastewater share. The S_I fractions prevailed (from 62.14% – R8 to 73.06% – R7). The X_S fraction constituted from 9.14% (R6) to 28.35% (R8), while the X_I fraction – from 6.80% (R7) to 9.51% (R8) (Table 2).

4 Conclusions

1. Fractions of insoluble hardly biodegradable compounds and undissolved compounds which are non-biodegradable were the prevailing COD fractions of dairy wastewater originating directly from the plant.
2. In raw wastewater the fraction of dissolved easily biodegradable compounds and the fraction of insoluble hardly biodegradable compounds prevailed, while in treated wastewater – the fraction of dissolved compounds which are not biologically decomposed, irrespective of the dairy wastewater share.
3. It was found that an increase in the percentage of dairy wastewater is accompanied by an increase in the value of the total COD and the fraction of insoluble hardly biodegradable compounds share.
4. Organic compounds belonging to the fraction of dissolved compounds which are not biologically decomposed were consumed by microorganisms directly, while those from the fraction of insoluble hardly biodegradable compounds had to be hydrolysed first.
5. Irrespective of the dairy wastewater share, a high efficiency of the use of organic compounds by microorganisms was ascertained (above 96.0%).

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