COD Fractions in Sewage Flowing into Polish Sewage Treatment Plants

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The paper presents the results of studies concerning the designation of COD fraction in raw wastewater. The research was conducted in three mechanical-biological sewage treatment plants. The results were compared with data assumed in the ASM models. During the investigation, the following fractions of COD were determined: dissolved non-biodegradable S_I, dissolved easily biodegradable S_S, in organic suspension slowly degradable X_S, and in organic suspension non-biodegradable X_I. The methodology for determining the COD fraction was based on the ATV- A 131guidelines. The real concentration of fractions in raw wastewater and the percentage of each fraction in total COD are different from data reported in the literature.

Key words:
COD fractions, raw wastewater, ASM models

Introduction

The application of modern technologies requires thorough identification of the composition of substrates present in sewage, as compared to data obtained with conventional pollution indicators (COD_{Cr}, BOD_5).[1–7] One of the most significant achievements in sewage technology is COD fractioning, which makes it possible to isolate fractions depending on the size of molecules and their responsiveness to biochemical decomposition. Determination of COD fractions furnishes a detailed characteristic of sewage composition, but primarily makes it possible to determine the amount of both easily and poorly degradable organic contaminants.[8–12]

The basic division of total COD in raw sewage into fractions used in designing and modelling of sewage treatment systems is presented in Fig. 1.[10,13,14]

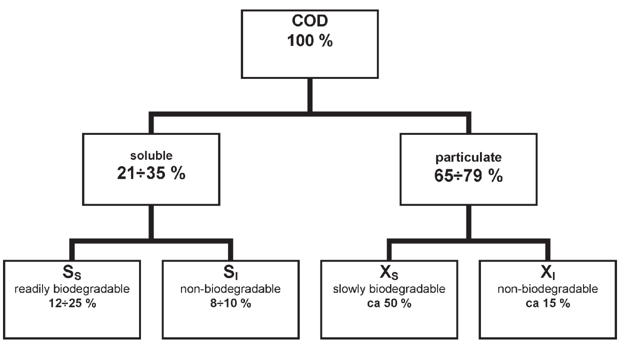

Fig. 1 – *Basic division of total COD in raw sewage into fractions*[10,13,14]

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Total COD values as the amount of individual fractions are dependent on the composition of sewage, and also on the applied method of separation of dissolved substances and suspensions. The reference data presented in Fig. 1 relating to the percentage ratio of COD fractions in household sewage show that the majority of total COD is contained in suspension (65–79 %). In this fraction, about 50 % of suspensions belong to slowly decomposing ones, whereas in the dissolved fraction of COD, the ratio of substances easily biodegradable has been estimated at 12–25 %. According to IAWQ (*International Association on Water Quality*), constituents occurring in a dissolved form are marked with an S, and in a non-dissolved form – with an X.[11] Therefore, depending on the form of occurrence of compounds, total COD will be the sum of:

$$COD_{tot.} = S_{COD} + X_{COD}\text{, g } O_2 \text{ m}^{-3} \quad (1)$$

where:

S_{COD} – the sum of dissolved organic substances, g O_2 m^{-3}

X_{COD} – the sum of organic substances in suspension, g O_2 m^{-3}

The IAWPRC (*International Association on Water Pollution Research and Control*) work group, currently *International Water Association* (IWA), has developed a universal mathematical model for designing an activated sludge process with the removal of nitrogen and phosphorus compounds.[15–17] The preliminary version of the model named ASM1 (*Activated Sludge* Model No.1) was published in 1987.[17,18] The ASM1 model enables the simulation of the processes of removal of organic compounds and nitrogen compounds from sludge with taking into account unit processes occurring both in the sewage and the active sludge.[16,18,19]

The constituent elements of total COD according to the ASM1 model are presented by equation (2):

$$COD_{tot.} = S_S + S_I + X_S + X_I + X_H + X_A + X_P \, . \quad \text{g O}_2 \text{ m}^{-3} \qquad (2)$$

where:

S_I – inert soluble organic material, g O_2 m^{-3}

S_s – soluble readily biodegradable substrates, g O_2 m^{-3}

X_I – inert particulate organic material, g O_2 m^{-3}

X_S – particulate slowly biodegradable substrates, g O_2 m^{-3}

X_H – heterotrophic organisms, g O_2 m^{-3}

X_A – autotrophic nitrifying organisms, g O_2 m^{-3}

X_P – decay products, g O_2 m^{-3}

Unless the biomass fraction is not included, this model is simplified to the form:

$$COD_{tot.} = S_S + S_I + X_S + X_I \, , \text{ g O}_2 \text{ m}^{-3} \qquad (3)$$

The ASM1 modifications have led to the formulation of successive versions: ASM2, ASM2d and ASM3.[15–18,20–22]

The division of organic substances in the ASM2 model is much more complex than in the ASM1 version.

The models assume that X_s and S_s are dominant in raw sewage fractions, whereas in lower concentrations two other fractions occur: S_I and X_I. The concentrations of the COD sewage fraction vary to a great degree and depend on the composition and origin of sewage.

The concentration value ranges of COD fractions in municipal sewage given in the literature are as follows:[17]

– total raw sewage COD 250–700 g O_2 m^{-3}
– soluble, easily biodegradable fraction (S_S) 25–125 g O_2 m^{-3}
– soluble, non-biodegradable fraction (S_I) 20–50 g O_2 m^{-3}
– insoluble, slowly biodegradable fraction (X_S) 200–400 g O_2 m^{-3}
– insoluble, non-biodegradable fraction (X_I) 35–110 g O_2 m^{-3}

The percentage ratios of the individual fractions in raw municipal sewage with the initial COD value = 300÷400 g O_2 m^{-3} according to the literature data, are as follows:[13]

– soluble, easily biodegradable fraction S_S 20÷25 %
– soluble, non-biodegradable fraction S_I 8÷10 %
– insoluble, slowly biodegradable fraction X_S 60÷65 %
– insoluble, non-biodegradable fraction X_I 5÷7 %

The percentage ratios of the COD fractions in raw municipal sewage according to the literature data are presented in Table 1.

T a b l e 1 – *COD ratios in raw sewage according to the literature data*

	S_I	S_S	X_I	X_S	X_H	X_S+X_H	VFA	Reference
	%							
	Raw wastewater							
South America	5.0	20.0	13.0			62.0		13
Switzerland	14.0	9.0	9.0	56.0	12.0	68.0		29
Denmark	2.0	20,0	18.0	40.0	20.0	60.0		30
Denmark	10.0	15.0	20.0	40.0	15.0	55.0	8.8	30
Spain	8.5	18.3	24.9	33.3	15.0	48.3		30
Sweden	15.0	27.0	17.0	33.0	8.0	41.0		31
Italy	6.0	15.0	8.0	56.0	15.0	71.0		30
Germany	6.1	14.8	13.0	55.4	10.8	66.2		30
Switzerland	4.0	10.0	20.0	54.1	11.9	66.0		32
North America	12.0	15.0	14.5			59.0	1.4	17
Germany	6.4	18.3	11.3	49.3	14.7	64.0		30
Denmark	7.6	20.3	13.0	51.5	7.2	58.7	8.1	2
North America	5.0	16.0	13.0			66.0	2.4	30
Denmark	5.0	35.0	10,0	35.0	15.0	50.0		30
France	4.1	3.0	19.0			73.9		30
North America	10.5	14.1	27.9			44.3	0.0	30
Hungary	4.6	21.9	23.7	49.9				30

The data collected in Table 1 indicated that the highest percentage ratios in the examined raw sewage are those of fractions X_S or X_S+X_H , and the lowest – fraction S_I. An analysis of the results given by the authors also shows that the ratio of biodegradable fractions expressed as the sum of X_S+S_S is above 70 %, which confirms the responsiveness of sewage to biodegradation.

The percentage ratios of the individual fractions presented in ASM1 and ASM2 models are shown in Table 2. In the ASM1 model, constant values of per-

Table 2 – *The percentage of COD fractions in the biokinetic models*[13,18,21]

COD fractions, %	The percentage of COD fractions in the biokinetic models	
	in ASM1 model	in ASM2 model
X_S	70	35–75
S_S	15	12–30
X_I	10	10–15
S_I	5	5–10

centage ratios of the individual fractions have been given, whereas in the ASM2 model, the ranges of percentage ratios of the individual fractions in total COD of raw sewage have been given.

Materials and methods

The goal of the research was to determine the real concentrations of COD fractions in raw sewage flowing into municipal sewage treatment plants in Poland. The results and calculations obtained have made it possible to determine percentage ratios of the individual fractions in total COD and compare the results obtained with the percentage ratios of the COD fractions presented in ASM1 and ASM2 models.

The characteristics of the research subjects

The research subjects were three municipal sewage treatment plants: for the cities of Zielona Góra, Sulechów and Nowa Sól. These are mechanical-biological sewage treatment plants with the function of the removal of nitrogen and phosphorus compounds, operating in low-load active sludge systems. The plant in Zielona Góra belongs to plants over 100 000 P.E. (People Equivalent), whereas the remaining two service between 15000 and 99999 P.E. The technology diagrams of the research subjects are presented in Fig. 2.

Research methodology

Raw (P1) and treated sewage samples (P2) were taken from each plant in spring (S), summer

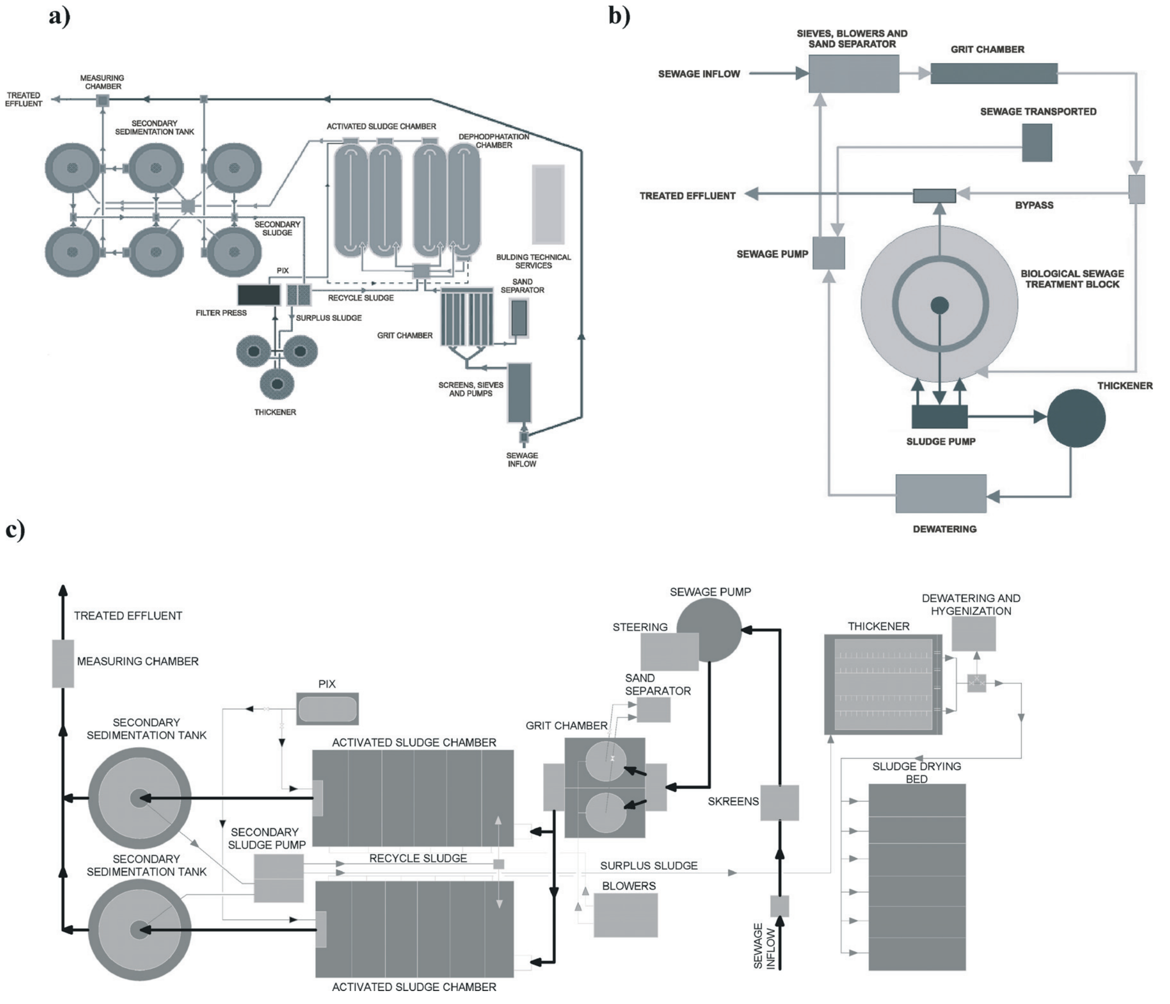


Fig. 2 – *Technology diagrams of the sewage treatment plants: a) Zielona Góra, b) Sulechów, c) Nowa Sól*

(Sm), autumn (A) and winter (W). The research was conducted in the plants in Zielona Góra and Sulechów from July 2005 to March 2006 and from July 2009 to March 2010, and in the plant in Nowa Sól from March 2008 to March 2010. The test sample was taken as the average daily sewage samples. The sewage samples were taken 6 times in each year season. During the research, from each sewage plant, 48 raw and 48 treated sewage samples were collected. Sewage sampling in the treatment plants was located at sewage inlets to the plants, and in the case of treated sewage at plant outlets. Raw and treated sewage samples were taken in accordance with PN-ISO 5667-10:1997.

The scope of physical-chemical analyses of sewage samples included the characterisation of:

– Chemical oxygen demand, COD – with the potassium dichromate method, as per PN-74/C-04578.03, PN-ISO 6060:2006,

– Biochemical oxygen demand, BOD – with the manometric method, using the OxiTop Control OC110 measurement system made by WTW,

– Total organic carbon, TOC – using the total organic carbon analyser TOC-V CSN made by Shimadzu,

– Dissolved organic carbon, DOC – using the total organic carbon analyser TOC-V CSN made by Shimadzu, in a sample of sewage filtered through a 0.45μm filter.

Laboratory analysis were performed in triplicate, in raw sewage samples and samples filtered through a 0.45μm filter.

Statistical verification of results was carried out using the STATISTICA 9.0. The results obtained in the study were determined basic descriptive statistics: arithmetic mean value and standard deviation what are presented in the charts boxed. The COD fraction methodology was developed on the basis of modified ATV-A131 guidelines.[23–26]

The methodology for the determination of fractions S_S, S_I, X_S and X_I involves characterisation of COD_{Cr} and BOD_5 in filtered and non-filtered samples of raw and treated sewage.

– The dissolved, non-biodegradable fraction S_I is termed as COD_{Cr} in filtered treated sewage.

– The dissolved, easily biodegradable fraction S_S is calculated from the difference of the concentration of dissolved organic contaminants S_{COD} determined in filtered raw sewage:

$$S_S = S_{COD} - S_I, \text{ g } O_2 \text{ m}^{-3} \quad (4)$$

– The slowly biodegradable organic fraction X_S is defined as the difference of total BOD (BOD_T), calculated based on the BOD_5 of non-filtered raw sewage and the biochemical decomposition coefficient (k_1 =0,6) and the dissolved, easily biodegradable fraction:

$$X_s = BOD_5/k_1 - S_S, \text{ g } O_2 \text{ m}^{-3} \quad (5)$$

– Non-biodegradable organic suspension X_I is determined from the dependence:

$$X_I = X_{COD} - X_s, \text{ g } O_2 \text{ m}^{-3} \quad (6)$$

where:

X_{COD} – total organic substance concentration in suspension,

– Total COD of raw sewage is determined as the sum of the fractions, with equation:

$$COD_{tot.} = S_I + S_S + X_S + X_I, \text{ g } O_2 \text{ m}^{-3}. \quad (7)$$

Results and discussion

The mean values of organic contaminant indicators calculated in different seasons for raw sewage and sewage treated in the sewage treatment plants: Zielona Góra, Sulechów and Nowa Sól are presented in Tab.3.

Sewage fed into the treatment plants in Zielona Góra, Sulechów and Nowa Sól differed with respect to the contaminant concentration ranges. The lowest contaminant index values characterised raw sewage flowing into the Zielona Góra treatment plant. The highest COD values in sewage were observed during the winter months. The mean values of the indices: COD, BOD_5 and TOC in raw sewage obtained during the research period have been presented in graphical form in Fig. 3.

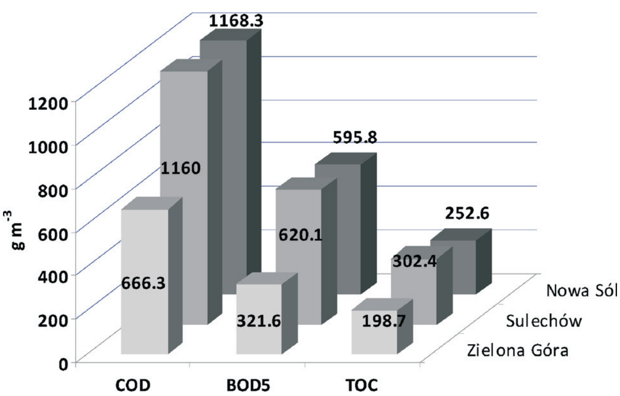


Fig. 3 – *The mean values of raw sewage in the municipal sewage treatment plants*

In the plants studied, the mean values of the indices COD_{Cr}, BOD_5 (Table 3, pts. P2) in treated sewage would correspond to the requirements for treated sewage given in the Regulation of the Minister of the Environment of 24 July 2006.

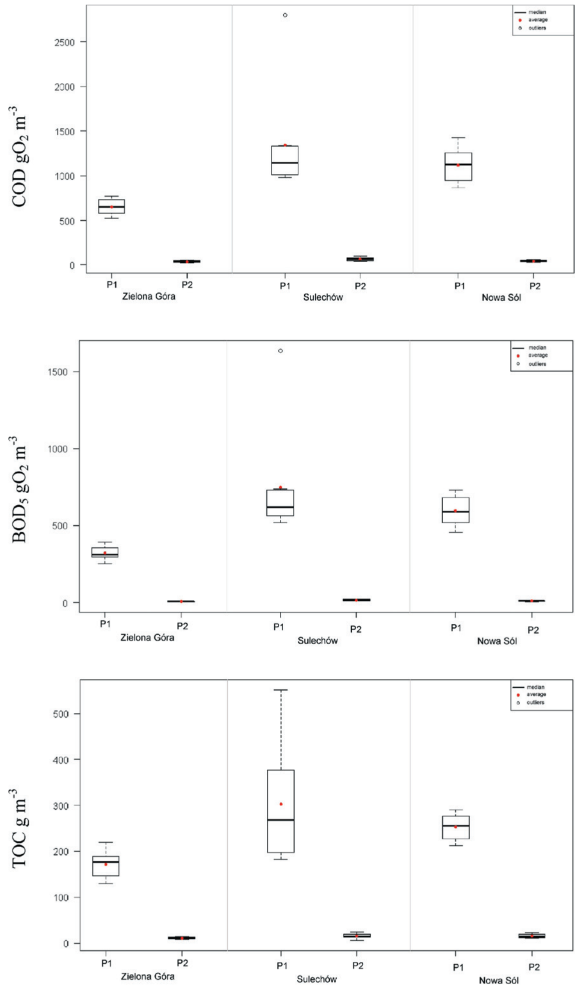
Table 3 – *The mean values of organic contaminant indicators calculated during different seasons in raw sewage and sewage treated in the municipal sewage treatment plants in Zielona Góra, Nowa Sól, Sulechów*

Season of the year	Sampling point	COD, g O_2 m^{-3}		BOD_5, g O_2 m^{-3}		TOC Unfiltered samples	DOC Filtered samples
		unfiltered samples	filtered samples	unfiltered samples	filtered samples	g C m^{-3}	
WWTP in Zielona Góra							
S	P1	661.0±83.4	220.0±17.0	320.0±0.0	197.0±117.4	178.6±11.1	52.0±17.3
	P2	43.0±7.1	32.0±5,7	5.9±0.7	4.0±0.6	14.1±0.7	10.8±0.9
Sm	P1	635.0±151.3	230.0±76.4	321.0±100.4	124.0±33.9	178.1±59.7	147.7±35.9
	P2	36.0±14.1	23.0±12.7	7.4±0.4	4.7±2.8	9.7±2.6	7.5±0.5
A	P1	667.0±142.8	200.0±22.6	298.5±7.8	126.2±8.,8	143.0±19.0	55.1±24.3
	P2	32.0±0.0	18.0±2.8	4.7±0.8	3.6±2.2	9.3±1.6	9.0±0.9
W	P1	702.0±110.3	214.0±25.5	347.0±66.5	100.5±0.7	186.1±6.9	73.7±48.5
	P2	51.0±1.1	36.0±0.0	6.7±1.9	4.6±1.3	10.8±0.6	9.4±0.5
WWTP in Sulechów							
S	P1	1160.0±226.3	285.0±7.1	584.0±50.9	189.0±14.1	317.0±190.0	174.7±90.7
	P2	68.0±0.0	40.0±0.0	13.5±0.7	11.0±0.0	13.1±1.4	11.3±1.1
Sm	P1	1011.0±41.0	235.0±21.2	548.5±44.5	243.5±61.5	267.9±0.2	161.8±0.5
	P2	39.0±1.4	19.0±1.4	10.7±0.4	9.0±0.0	15.2±0.1	12.6±0.1
A	P1	1219.0±140.0	317.0±63.8	679.0±83.4	242.0±11.3	198.0±2.8	96.9±38.6
	P2	53.0±7.1	32.0±0.0	15.9±2.6	7.4±3.7	9.7±5.6	8.7±6.6
W	P1	2070.0±1032.4	600.0±282.8	1177.5±649.8	301.0±142.8	426.8±176.6	221.9±59.5
	P2	95.0±4.2	46.0±2.8	24.0±0.0	4.7±0.1	23.0±1.2	10.2±1.5
WWTP in Nowa Sól							
S	P1	1006.0±195.2	347.0±26.9	520.0±56.6	271.0±55.2	231.5±27.6	139.5±4.8
	P2	60.0±2.8	30.0±2.8	13.5±2.1	10.0±2.8	21.7±2.2	20.0±0.1
Sm	P1	1229.0±108.9	435.0±32.5	655.0±106.1	409.0±43.8	265.8±34.2	160.8±21.7
	P2	36.0±5.7	26.0±8.5	5.0±1.4	4.0±1.4	11.1±0.3	10.3±0.1
A	P1	1392.0±50.9	437.0±117.4	680.0±42.4	254.0±19.8	276.3±4.5	148.4±62.6
	P2	46.5±6.4	30.0±2.8	9.0±2.8	5.5±3.5	11.4±0.4	10.1±0.3
W	P1	1046.0±149.9	386.0±14.1	528.0±101.8	271.0±58.0	236.7±34.1	158.4±4.6
	P2	50.0±2.8	32.0±0.0	10.0±1.4	5.7±3.3	18.0±0.1	17.2±1.0

The ranges of concentrations of organic pollutants expressed by indicators COD, BOD and TOC in raw and treated sewage are shown graphically in charts boxed in Fig.4.

The results of the statistical analysis presented in Fig. 4, confirm compatibility of the results of COD, BOD_5 and TOC in the treated sewage from Zielona Góra, Sulechów and Nowa Sól . This is confirmed by the narrow space between the upper and lower quartiles in the chart. Concentrations of organic pollutant indicators in raw sewage were more varied, which is confirmed by the wide space between the upper and lower quartiles in the chart. In the Sulechów plant were found outlier results for BOD_5 and COD.

In accordance with the procedure for determining the COD fraction given in point 3, the concentrations of the individual fractions for raw and treated sewage flowing into the tested plants have been calculated.



F i g . 4 – *Concentration ranges of organic pollutants expressed by indicators COD, BOD_5 and TOC in raw and treated sewage*

The mean concentrations of the COD fraction in raw and treated sewage in the tested treatment plants are presented in Table 4.

The results of the research show that in raw sewage, the most concentrated are fractions X_S and S_S. Definitely lower are the concentrations of fractions X_I and S_I. The most important concentrations among the calculated fractions characterised the undissolved, slowly biodegradable organic fraction (X_S).

An analysis of the COD fraction of raw sewage flowing into the studied treatment plants has shown that the highest concentrations characterised fractions X_S and S_S. The concentrations of these fractions were:

in sewage in Zielona Góra
X_S 347.3±56.1 g O_2 m^{-3}; S_S 188.8±38.0 g O_2 m^{-3}
in sewage in Nowa Sól
X_S 620.1 ± 141.3 g O_2 m^{-3}; S_S 371.8±62.6 g O_2 m^{-3}
in sewage in Sulechów
X_S^* 770.1±118.1 g O_2 m^{-3}; S_S^* 263.4± 55.4 g O_2 m^{-3}

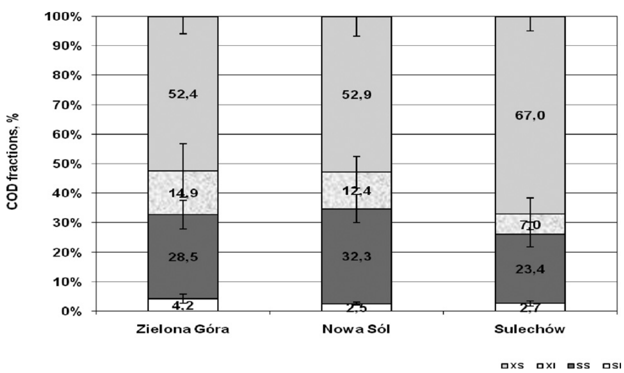
*without taking into account the results from winter of 2010

On the other hand, the lowest were the concentrations of fraction S_I (dissolved, non-biodegradable substances), which were: in sewage in Zielona Góra – 27.3±9.3 g O_2 m^{-3}, in sewage in Sulechów – 34.3±10.9 g O_2 m^{-3} and 29.5±4.2 g O_2 m^{-3} in sewage in Nowa Sól.

In the Nowa Sól treatment plant, the percentage ratio of fraction X_I in raw sewage was at 4.4–18.1 %, in Sulechów 1.0–18.7 %, and in Zielona Góra – 6.8–21.0 %. The results obtained in the study have shown a differentiated, often greater than 15 % ratio of fraction X_I in raw sewage in the studied treatment plants.

The lowest ratio of total COD of the tested raw sewage was of fraction S_I. In the sewage of Zielona Góra, it was 4.2±1.6 %, Sulechów – 2.7±0.9 % and in Nowa Sól it was 2.5±0.5 %.

In the raw sewage from Zielona Góra, Sulechów and Nowa Sól, despite the individual COD fractions, consistency in terms of the order of occurrence of the individual fractions in total COD was found. The average ratio of the individual COD fractions in raw sewage from Zielona Góra, Sulechów and Nowa Sól are presented in graphical form in Fig.5.



F i g . 5 – *Average percentage ratio of the individual COD fractions in raw sewage*

The ratios of the individual COD fractions in raw sewage differ from the percentage fraction ratios given in the literature (Tables 1, 2).

Both the results of our research and those of other authors, collected in Table 6, confirm the low content of dissolved, non-biodegradable contaminants, and a definite majority of the suspension fractions in relation to dissolved fractions in raw sewage.

Mejer [27,28] reported that in raw sewage with the COD at 603.9±95.5 g O_2 m^{-3} flowing into the Hardenberg treatment plant, the ratio of fraction S_S was 33.1 % and of fractions X_S, S_I and X_I – 31.3, 6.6 and 29.0 %, respectively. These results also confirm that the dominant fractions in raw sewage are fractions S_s and X_s.

Table 4 – *Mean concentrations of the COD fraction of sewage in Zielona Góra, Sulechów and Nowa Sól*

Season of the year	Sampling point	COD fractions, g O_2 m^{-3}				Total COD g O_2 m^{-3}
		S_I	S_S	X_S	X_I	
		WWTP in Zielona Góra				
S	P1	32.0±5.7	188.0±11.3	345.0±11.3	96.0±77.8	661.0±83.4
	P2	32.0±5.7	0.0±0.0	10.0±1.4	1.0±0.0	43.0±7.1
Sm	P1	23.0±12.7	207.0±89.1	328.0±77.8	77.0±2.8	635.0±151.3
	P2	23.0±12.7	0.0±0.0	12.0±1.4	1.0±0.0	36.0±14,1
A	P1	18.0±2.8	182.0±19,8	315.5±6.4	151.5±159.1	667.0±142.8
	P2	18.0±2.8	0.0±0.0	7.8±1.1	5.9±4.4	32.0±0.0
W	P1	36.0±0.0	178.0±25,5	400.3±85.3	87.5±0.7	702.0±110.3
	P2	36.0±0.0	0.0±0.0	11.1±3.2	4.0±4.2	51.0±1.1
		WWTP in Sulechów				
S	P1	40.0±0.0	245.0±7.1	728.0±91.9	147.0±141.4	1160.0±226.3
	P2	40.0±0.0	0.0±0.0	22.5±0.7	5.5±0.7	68.0±0.0
Sm	P1	19.0±1.4	216.0±19.8	698.5±54.4	77.5± 34.6	1011.0±41.0
	P2	19.0±1.4	0.0±0.0	17.5±0.7	2.5±0.7	39.0±1.4
A	P1	32.0±0.0	285.0±63.6	846.5±202.9	55.5±0.7	1219.0±140.0
	P2	32.0±0.0	0.0±0.0	18.0±7.1	3.0±0.0	53.0±7.1
W	P1	46.0±2.8	554.0±285.7	1408.5±796.9	61.5±47.4	2070.0±1032.4
	P2	46.0±2.8	0.0±0.0	40.0±0.0	9.0±1.4	95.0±4.2
		WWTP in Nowa Sól				
S	P1	30.0±2.8	317.0±24.0	549.5±70.0	109.5±98.3	1006.0±195.2
	P2	30.0±2.8	0.0±0.0	22.5±3.5	7.5±3.5	60.0±2.8
Sm	P1	26.0±8.5	409.0±41.0	683.0±217.8	111.0±76.4	1229.0±108.9
	P2	26.0±8.5	0.0±0.0	8.5±2.1	1.5±0.7	36.0±5.7
A	P1	30.0±2.8	407.0±114.6	726.0±43.8	229.0±22.6	1392.0±50.9
	P2	30.0±2.8	0.0±0.0	15.0±4.2	1.5±0.7	46.5±6.4
W	P1	32.0±0.0	354.0±14.1	522.0±161.2	138.0±25.5	1046.0±149.9
	P2	32.0±0.0	0.0±0.0	16.5±2.1	1.5±0.7	50.0±2.8

The values of the individual fraction ratios presented in the biokinetic ASM1 and ASM2 models are collected in Table 7. In this table are also presented results obtained in operational sewage treatment plants in Zielona Góra, Sulechów and Nowa Sól.

The determined values of the percentage ratios of the individual fractions differ from the values presented in ASM1 and ASM2 models. The research has shown that the highest concentrations in raw sewage are, in descending order, those of fraction X_S, then S_S, X_I and S_I.[23–25]

Such an order of the concentrations appears in models ASM. Significant differences between actual research and values given in ASM models pertain to the content range of the individual fractions. The research has revealed higher percentage ratios of fractions X_I and S_S, as compared to the values in the ASM1 and ASM2 models, and lower percentage ratios of fractions S_I and X_S.

In biokinetic ASM models it is given that the concentrations of the non-biodegradable fractions (S_I and X_I) in the process line of a sewage treatment plant do not change or change insignificantly.

T a b l e 5 – *Average percentage ratios of the fractions in the COD of raw sewage in the treatment plants in Zielona Góra, Sulechów and Nowa Sól*

Season of the year	Sampling point	COD fractions, %			
		S_I	S_S	X_S	X_I
		WWTP in Zielona Góra			
S	P1	4.8±0.2	28.6±1.9	52.7±8.4	13.9±10.0
	P2	74.3±0.9	0.0±0.0	23.3±0.5	2.4±0.4
Sm	P1	4.0±3.0	31.8±6.4	51.7±0.1	12.5±3.4
	P2	61.7±11.1	0.0±0.0	35.3±9.9	3.0±1.1
A	P1	2.8±1.0	28.3±9.0	48.3±9.4	20.6±19.4
	P2	56.3±8.8	0,0±0.0	25.0±4.4	18.8±13.2
W	P1	5.2±0.8	25.4±0.4	56.8±3.3	12.6±2.1
	P2	70.6±2.0	0.0±0.0	21.7±6.1	7.7±8.1
		WWTP in Sulechów			
S	P1	3.5±0.7	21.6 ±4.8	63.2±4.4	11.7±9.9
	P2	58.8±0.0	0.0±0.0	33.1±1.0	8.1±1.0
Sm	P1	1.9±0.1	21.3±1.1	69.0±2.6	7.7±3.7
	P2	48.7±1.9	0.0±0.0	44,9±0.2	6.4±2.0
A	P1	2.6±0.3	23.8±8.0	68.9±8.7	4.6±0.5
	P2	60.9±8.1	0.0±0.0	33.4±8.9	5.7±0.8
W	P1	2.6±1.4	26.6±0.5	66.7±5.2	4.0±4.3
	P2	48.4±0.8	0.0±0.0	42.1±1.9	9.4±1.1
		WWTP in Nowa Sól			
S	P1	3.0±0.3	31.9±3.8	55.0±3.7	10.1±7.8
	P2	49.9±2.4	0.0±0.0	37.4±4.1	12.7±6.5
Sm	P1	2.1±0.5	33.6±6.3	55.0±12.8	9.3±7.0
	P2	71.3±12.4	0.0±0.0	24.4±9.7	4.4±2.6
A	P1	2.2±0.1	29.1±7.2	52.2±5.1	16.5±2.2
	P2	64.7±2.8	0.0±0.0	31.9±4.7	3.4±1.9
W	P1	3.1±0.4	34.1±3.5	49.3±8.3	13.5±4.4
	P2	64.1±3.6	0.0±0.0	32.9±2.4	3.0±1.2

T a b l e 6 – *COD fraction ratio in raw sewage (own and literature data)*

COD fractions,%	WWTP			Kalinowska, Oleszkiewicz[33]	Kappeler, Gujer[29]	Henze[34]	Pasztor[30]	Ekama[13]	Hellstedt[35]
	Zielona Góra	Sulechów	Nowa Sól						
	raw wastewater								
S_S	28.5±4.9	23.4±4.2	32.3±4.7	12–25	10–20	24–32	21.9	20–25	21.8
S_I	4.1±1.6	2.7±0.9	2.5±0.5	8–10	7–11	8–11	4.6	8–10	8
X_S	52.4±5.9	67.0±5.0	52.9±6.7	50	53–60	43–49	49.8	35–60	62
X_I	14.9±9.1	7.0±5.4	12.4±5.3	15	7–15	11–20	23.7	5–7	8.2

Table 7 – *Percentage COD fraction ratio in raw sewage according to own research and the values presented in the ASM1 and ASM2 models*

COD fractions,%	Zielona Góra	Sulechów	Nowa Sól	ASM1	ASM2
	raw wastewater				
S_I	1.9 – 6.1	1.6 –4.0	1.7 – 3.4	5	5-10
S_S	21.9 – 36.4	18.2 – 29.0	24.0 – 38.0	15	12-30
X_I	6.9 – 21.0	1.0 – 18.7	4.6 – 18.1	10	10-15
X_S	41.7 – 59.1	60.1 – 75.1	43.4 – 64.1	70	35-75

It has been written that fraction S_I is present in raw sewage and may be formed in the process of hydrolysis of fraction X_S.[15–17] Because of this, the concentration of fraction S_I in treated sewage is equal to or slightly higher than the concentrations of this fraction in raw sewage. The research conducted in the Zielona Góra, Sulechów and Nowa Sól treatment plants showed that in raw sewage the concentration of fraction S_I was 14–48 g O_2 m^{-3} and did not change throughout the process lines of the plants.

The percentage ratios of the non-biodegradable fractions ($COD_I = S_I + X_I$) in raw sewage in the studied plants was between 2.6 and 36.5 %, whereas Sperandio[6] had observed that in raw sewage the ratios of these fractions were 20 %.

Conclusions

Data on the concentrations of COD fractions in raw sewage have been presented in numerous publications, but most often they are the result of computer simulations.

The research conducted has made it possible to determine the individual COD fractions in raw sewage flowing into the treatment plants studied. The results obtained are consistent with literature data which show that the highest concentrations characterise fractions X_S and S_S.

The concentrations of these fractions in raw sewage in the studied plants were as follows:

in sewage in Zielona Góra
X_S 347.3±56.1 g O_2 m^{-3}; S_S 188.8±38.0 g O_2 m^{-3},

in sewage in Nowa Sól
X_S 620.1±141.3 g O_2 m^{-3}; S_S 371.8±62.6 g O_2 m^{-3},

in sewage in Sulechów
X_S 770.1±118.1 g O_2 m^{-3}; S_S 263.4±55.4 g O_2 m^{-3}.

In raw sewage, the lowest were the concentrations of fractions S_I (non-biodegradable dissolved substances). In raw sewage from Zielona Góra, the concentration of fraction S_I was calculated at 27.3±9.3 g O_2 m^{-3} , in sewage from Sulechów – 34.3±10.9 g O_2 m^{-3} , and 29.5±4.2 g O_2 m^{-3} in sewage from Nowa Sól.

In raw sewage, the determined concentrations of fraction X_I were:

Zielona Góra

$$X_I = 103.0 \pm 73.7 \text{ g } O_2 \text{ m}^{-3}$$

Nowa Sól

$$X_I = 146.9 \pm 71.4 \text{ g } O_2 \text{ m}^{-3}$$

Sulechów

$$X_I = 85.4 \pm 69.8 \text{ g } O_2 \text{ m}^{-3}$$

Based on the research results, the percentage ratios of the individual fractions in total COD of raw sewage have been determined. The percentage ratios of the individual fractions have been estimated in the intervals:

$$S_S = 23.4 \pm 4.2 \text{ to } 32.3 \pm 4.7 \ \%$$

$$S_I = 2.5 \pm 0.5 \text{ to } 4.1 \pm 1.6 \ \%$$

$$X_S = 52.4 \pm 5.9 \text{ to } 67.0 \pm 5.0 \ \%$$

$$X_I = 7.0 \pm 5.4 \text{ to } 14.9 \pm 9.1 \ \%$$

The test results confirm the low content of non-biodegradable dissolved contaminants in raw sewage and a definite majority of the suspension fractions in comparison to the dissolved fractions.

The values of the percentage ratios of the individual fractions determined by the research differ from values given in ASM models. The research has shown that the fraction occurring in the highest concentration in raw sewage is X_S, followed by S_S, X_I and S_I. Such an order is present in biokinetic models. Significant differences between actual research and values given in models pertain to the content range of the individual fractions. The research has revealed higher percentage ratios of fractions X_I and S_S, as compared to the values in the ASM1 and ASM2 models, and lower percentage ratios of fractions S_I and X_S.

In raw sewage flowing into the treatment plants in Zielona Góra, Sulechów and Nowa Sól predominated biochemically degradable organic contaminants, expressed as fractions S_S and X_S.

In the literature, the sum of these fractions is marked as COD_S ($COD_S = S_S + X_S$).

The highest ratios of these fractions have been observed in raw sewage flowing into the treatment plant in Sulechów, in which the COD fractions constituted 90.3±5.7 % of total COD of the sewage.

In raw sewage from Zielona Góra, the percentage ratio of the COD_S fraction was 80.9±8.9 %. Slightly lower ratios of fractions S_S and X_S, at 85.0±5.2 %, were observed in raw sewage from Nowa Sól.

Among biodegradable fractions in raw sewage, fraction X_S, which characterises slowly degradable suspensions is predominant. The research on the concentrations of fractions S_S and S_I in sewage before and after biological treatment processes conducted by Dulekgugen[8], shows that treated sewage contains fraction S_I and fraction S_P, defined as dissolved inert metabolites produced in the process of biological treatment. The authors report that in treated sewage, fraction S_S does not occur.

In treated sewage flowing out of the analysed plants, fraction S_S was not found, and thus the level of removal of dissolved easily biodegradable organic contaminants defined using fraction S_S was very high and can be assumed at >99.9 %. The results obtained are consistent with the assumption that easily biodegradable contaminants are wholly consumed by active sludge microorganisms.

The average ratios of suspension fractions X_S and X_I in treated sewage:

in Zielona Góra were at
X_S 10.2±2.0 g O_2 m^{-3} and X_I 3.1±3.2 g O_2 m^{-3}

in Nowa Sól at
X_S 15.6±5.8 g O_2 m^{-3} and X_I 3.0±3.1 g O_2 m^{-3}

whereas higher values of suspension fractions at X_S 24.5±10.2 g O_2 m^{-3} and X_I 5.0±2.8 g O_2 m^{-3} characterised treated sewage in the Sulechów treatment plant.

The results of the content of the treated degradable fractions X_S and S_S in treated sewage are evidence of the high efficiency of the studied plants in the removal of biodegradable organic contaminants.

The research results presented in the paper along with their interpretation make it possible to draw the following final conclusions:

1. Total COD, as compared to BOD_5, COD_{Cr} or TOC, is a better indicator of the organic contaminant content, because it enables determination of the concentrations of biodegradable and non-biodegradable fractions, dissolved and suspended.

2. The percentage ratios of the individual fractions in raw sewage determined in actual conditions differ from the data given in the literature.

3. Research on sewage composition conducted in real plants has shown a significant difference between the actual parameters and data given in ASM models.

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