

COD FRACTIONS IN RAW AND MECHANICALLY TREATED WASTEWATER

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The paper presents results of studies concerning the designation of COD fraction in the raw and mechanically treated wastewater in different year seasons. The research object was a mechanical-biological wastewater treatment plant with the output of >40 000 P.E., located in western Poland. The results of COD fraction in the raw wastewater were compared with data received in the ASM models. Methodology for determining the COD fraction was based on the guidelines ATV - A 131. During the research following fractions were determined: particulate slowly biodegradable substrates (X_S), soluble readily biodegradable substrates (S_S), inert particulate organic material (X_I) and inert soluble organic material (S_I). Soluble and particulate components were differentiated by filtration through 0.45 μ m membrane filters. The percentage of each fraction in total COD determined on the real concentration in raw wastewater are different from data reported in the literature.

Keywords: raw wastewater; COD fractions; ASM models; organic substances biodegradable and non-biodegradable

1. INTRODUCTION

The diversity of unit biochemical processes occurring in integrated removal of contaminants from wastewater has had an impact on the application of computer simulations based on various mathematical models in designing [5,13,19]. The application of these methods requires, however, more detailed data on the wastewater content, as compared to the values of conventional indices, such as BOD_5 , COD_{Cr} , COD_{Mn} , TOC or ignition loss. Also the knowledge of many kinetic parameters of kinetic unit processes is required. In the design and optimisation of biological wastewater treatment processes, it is very important

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to determine the biodegradability of contaminants with taking into account the ratios of contained by them compounds responsive and resistant to decomposition, and the influence of wastewater constituents on the course of unit processes. Detailed characterisation of organic contaminants is of increasing significance also in sludge stabilisation processes and problems related to sludge liquors forming in wastewater treatment plants [5,11,12,17]. The index BOD₅, so commonly used in designing technology wastewater treatment systems, only provides information about easily biodegradable contaminant content, however, it does not, take into account the amount of non-biodegradable contaminants which lower the effectiveness of biological wastewater treatment. The index COD, with division into fractions, is currently presented as the most appropriate for the characterisation of organic substrates present in wastewater, because it makes it possible to obtain information on biodegradability of organic contaminants, both in dissolved and suspension form [1,3,15,23,24].

According to the IAWQ (*International Association on Water Quality*) nomenclature, dissolved constituents are marked with the symbol S and undissolved ones with the symbol X [8]. Depending on the form of compounds, total COD will be the sum of:

$$COD_{tot.} = S_{COD} + X_{COD}, gO_2 / m^3 \quad (1.1)$$

where: S_{COD} – the sum of dissolved organic substances, gO_2/m^3

X_{COD} – the sum of organic substances in suspension, gO_2/m^3 .

The percentage ratio of the suspension fraction in total COD of raw household wastewater is 65÷79% and dissolved – 21÷35. It is also assumed that the percentage ratio of suspensions in household wastewater is about 57% COD and colloids and dissolved substances about 43% in total [4,6,16,18].

2. COD FRACTION CONCENTRATIONS IN BIOKINETIC ASM MODELS

The IAWPRC (*International Association on Water Pollution Research and Control*) work group, currently *International Water Association* (IWA), was appointed in 1982, in order to develop a universal mathematical model for designing the activated sludge process with the removal of nitrogen and phosphorus compounds [6,7,15,25].

The preliminary version of the model named (*Activated Sludge Model No.1*) was published in 1987 [10,15]. ASM1 model enables the simulation of the processes of removal of organic compounds and nitrogen compounds from wastewater, with taking into account unit processes which occur both in wastewater, as well as active sludge [7,10,14].

The model includes eight unit processes which are divided into 3 groups:

- hydrolysis processes involving:
 - organic compound hydrolysis under non-limiting oxygen conditions,
 - organic compound hydrolysis under oxygen-free conditions,
 - organic nitrogen hydrolysis,
- organic substance decomposition processes occurring in the presence of heterotrophic bacteria (X_H):
 - heterotrophic biomass growth under non-limiting oxygen conditions,
 - heterotrophic biomass growth under anoxic conditions,
 - heterotrophic biomass decomposition,
- processes conducted by autotrophic bacteria (nitrificants) (X_A):
 - autotrophic biomass growth under non-limiting oxygen conditions,
 - autotrophic biomass decomposition.

The constituents of total COD according to the ASM1 model are presented by the equation:

$$COD_{tot.} = S_S + S_I + X_S + X_I + X_H + X_A + X_P, gO_2 / m^3 \quad (2.1)$$

where:

S_I – inert soluble organic material, gO_2/m^3

S_S – soluble readily biodegradable substrates, gO_2/m^3

X_I – inert particulate organic material, gO_2/m^3

X_S – particulate slowly biodegradable substrates, gO_2/m^3

X_H – heterotrophic organisms, gO_2/m^3

X_A – autotrophic nitrifying organisms, gO_2/m^3

X_P – decay products, gO_2/m^3 .

Unless the biomass fraction is included, this model is simplified to the form:

$$COD_{tot.} = S_S + S_I + X_S + X_I, gO_2 / m^3 \quad (2.2)$$

ASM1 modifications have led to the creation of subsequent versions: ASM2, ASM2d and ASM3 [2,6,7,8,9,15]. Thus, the ASM1 model, which describes only the removal of organic compounds and nitrogen compounds, has been expanded to a version covering advanced phosphorus removal processes. A novelty in the ASM2 model is the isolation from the group of active sludge microorganisms (PAO's) ones with the ability of phosphorus cumulation by polyphosphate storage [6,8,10].

The concentrations of the individual COD fractions according to the ASM1 and ASM2 models are the following [4,6,8,9,10]:

| ASM1 | | ASM2 | |
|---|-------------------------------------|---|-------------------------------------|
| COD_{tot} = 400 gO₂/m³ | | COD_{tot} = 263 gO₂/m³ | |
| X _S particulate slowly biodegradable substrates: | 280 gO ₂ /m ³ | X _S particulate slowly biodegradable substrates: | 125 gO ₂ /m ³ |
| S _S soluble readily biodegradable substrates: | 60 gO ₂ /m ³ | S _F fermentable, readily biodegradable organic substrates: | 30 gO ₂ /m ³ |
| X _I inert particulate organic material: | 40 gO ₂ /m ³ | X _I inert particulate organic material: | 25 gO ₂ /m ³ |
| S _I inert soluble organic material: | 20 gO ₂ /m ³ | S _I inert soluble organic material: | 30 gO ₂ /m ³ |
| | | S _A fermentation products (acetate): | 20 gO ₂ /m ³ |
| | | X _H heterotrophic organisms: | 30 gO ₂ /m ³ |
| | | X _A autotrophic nitrifying organisms: | 1 gO ₂ /m ³ |
| | | X _{PAO} Phosphorus Accumulating Organisms PAO: | 1 gO ₂ /m ³ |
| | | X _{PHB} cell internal storage product of PAO's: | 1 gO ₂ /m ³ |

The division of organic substances in the ASM2 model is much more complex than in the ASM1 version, because it takes into account 19 constituents used in wastewater and active sludge characterisation. Ten of them relate to insoluble constituents, nine to soluble ones [6,9,10].

The models assume that in raw wastewater fractions X_s and S_s are dominant, whereas in lower concentrations two other fractions occur: S_I and X_I. The percentage ratios of the individual fractions assumed by the ASM1 and ASM2 models are presented below:

| ASM1 | | ASM2 | |
|---|------|---|-----------|
| X _S particulate slowly biodegradable substrates: | 70 % | X _S particulate slowly biodegradable substrates: | 35 ÷ 75 % |
| S _S soluble readily biodegradable substrates: | 15 % | S _S soluble readily biodegradable substrates: | 12 ÷ 30 % |
| X _I inert particulate organic material: | 10 % | X _I inert particulate organic material: | 10 ÷ 15 % |
| S _I inert soluble organic material: | 5 % | S _I inert soluble organic material: | 5 ÷ 10 % |

The ASM1 model assumes constant values of the percentage ratio of the individual fractions, whereas the ASM2 model gives ranges of percentage ratios of the individual fractions in total COD of raw wastewater.

3. METHODOLOGY OF COD FRACTION DETERMINATION

The methodology of COD fraction determination has been developed on the basis of the ATV-A131 guidelines [20,21,22,26]. The methodology for the determination of the fractions involves the characterisation of COD and BOD₅ in filtered and non-filtered samples of raw and treated wastewater.

- The dissolved, non-biodegradable fraction S_I is termed as COD in filtered treated wastewater.

- 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 wastewater and the concentration of the dissolved non-biodegradable fraction (S_I):

$$S_S = S_{COD} - S_I, gO_2 / m^3 \quad (3.1)$$

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

$$X_S = \frac{BOD}{k_1} - S_S, gO_2 / m^3 \quad (3.2)$$

for household wastewater, it is assumed that $k_1=0.6, 1/d$.

- Non-biodegradable organic suspension X_I is calculated from the dependence:

$$X_I = X_{COD} - X_S, gO_2 / m^3 \quad (3.3)$$

where: X_{COD} is total concentration of dissolved organic substances in suspension.

- Total COD of raw wastewater as the sum of the fractions is determined with the equation:

$$COD_{tot.} = S_S + S_I + X_S + X_I, gO_2 / m^3 \quad (3.4)$$

Soluble and particulate components were differentiated by filtration through $0.45\mu m$ membrane filters.

4. THE GOAL AND SCOPE OF THE RESEARCH

The goal of the research was to determine the actual concentrations of COD fractions in raw wastewater flowing into a municipal wastewater treatment plant with the output of $15000 m^3/d$. 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 assumptions of the biokinetic ASM1 and ASM2 models. It was also investigated the effect of mechanical treatment in grit chamber into the COD fractions changes. This part of the study was to test how the process of mineral suspended solids separate will affect on the participation of the COD fractions.

4.1. The characteristic of the research subject

The research object was a municipal wastewater treatment plant with the output of >40 000 P.E., located in western Poland. It is a mechanical-biological wastewater treatment plant with the function of the nitrogen and phosphorus compounds removal.

During the research following wastewater samples were collected: raw wastewater, wastewater after grit chamber and treated wastewater. The technology diagram of the research object is presented in Fig. 1.

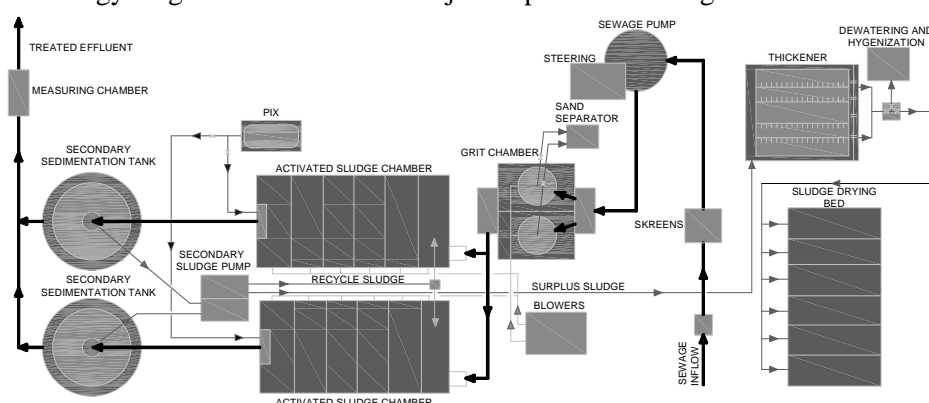


Fig. 1. The technology diagram of the WWTP

4.2. Testing methodology

Raw and treated wastewater samples were taken in accordance with PN-ISO 5667-10:1997.

The scope of physical-chemical analyses of wastewater 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 wastewater filtered through a 0.45µm filter.

The characterisations were conducted in three repetitions, in raw wastewater samples and samples filtered through a 0.45µm filter.

The obtained research results were statistically analyzed using Statistica 9.0. Determined following statistical values: the arithmetic mean, median, maksimum value, minimum value and standard deviation.

5. TEST RESULTS

In the testing period, the organic contaminant values in raw wastewater were: COD = 868.0-1428.0 gO₂/m³, BOD₅ = 456.0-730.0 gO₂/m³, TOC = 212.0-290.0 gC/m³, while in the wastewater after grit chamber were: COD = 566.0-920.0 gO₂/m³, BOD₅ = 288.0-494.0 gO₂/m³ and TOC = 135.8-234.1 gC/m³.

The test results of raw wastewater composition and its changes after grit chamber as mean values are presented in Table 1. The test results correlated in Table 1 suggest that in the analysed period encompassing different seasons, the composition of raw wastewater flowing into the WWTP did not vary significantly.

Table 1. Organic contaminants in raw wastewater and in wastewater after grit chamber

| Wastewater samples | COD, gO ₂ /m ³ | | BOD ₅ , gO ₂ /m ³ | | TOC Unfiltered samples | DOC Filtred samples |
|-------------------------------|--------------------------------------|-----------------|--|-----------------|---------------------------|------------------------|
| | Unfiltered samples | Filtred samples | Unfiltered samples | Filtred samples | gC/m ³ | |
| Raw wastewater | 1143.3±187.1 | 401.3±62.0 | 595.8±98.9 | 301.3±75.7 | 252.6±29.2 | 151.8±26.7 |
| Wastewater after grit chamber | 775.8±127.4 | 354.5±82.2 | 401.5±75.1 | 201.9±69.3 | 194.4±34.3 | 104.0±15.9 |

The wastewater was characterised by a mean COD value of 1143.3±187.1 gO₂/m³ and a mean BOD₅ value of 595.8±98.9 g O₂/m³. Wastewater treatment in grit chamber resulted in a decrease concentration of organic pollutants average of 30%.

In accordance with the procedure for determining the COD fraction given in point 3, the concentrations of the individual fractions in the effluent and mechanically treated wastewater in analysed wastewater treatment plant have been calculated. The results showing the concentrations of the individual fractions are presented in Table 2.

Table 2. The COD fraction concentrations in raw wastewater (P1) and in wastewater after grit chamber (P2)

| Season of the year | | COD fractions, gO ₂ /m ³ | | | |
|--------------------|----|--|----------------|----------------|----------------|
| | | S _I | S _S | X _S | X _I |
| Spring | P1 | 30.0±2.8 | 317.0±24.0 | 549.5±70.0 | 109.5±98.3 |
| | P2 | 30.0±2.8 | 277.0±15.6 | 281.5±95.5 | 75.5±24.7 |

| | | | | | |
|--------|----|----------|-------------|-------------|------------|
| Summer | P1 | 26.0±8.5 | 409.0±41.0 | 683.0±217.8 | 111.0±76.4 |
| | P2 | 26.0±8.5 | 445.0±38.2 | 356.5±40.3 | 71.5±19.1 |
| Autumn | P1 | 30.0±2.8 | 407.0±114.6 | 726.0±43.8 | 229.0±22.6 |
| | P2 | 30.0±2.8 | 330.0±31.1 | 395.0±107.5 | 102.0±52.3 |
| Winter | P1 | 32.0±0.0 | 354.0±14.1 | 522.0±161.2 | 138.0±25.5 |
| | P2 | 32.0±0.0 | 248.0±28.3 | 339.5±21.9 | 63.5±17.7 |

S_I inert soluble organic material, S_S soluble readily biodegradable substrates, X_S particulate slowly biodegradable substrates, X_I inert particulate organic material

During the research found a high variability of wastewater parameters, which reflect the values of the standard deviation.

The test results show that in raw wastewater, the most concentrated are fractions X_S and S_S . Definitely lower are the concentrations of fractions X_I and S_I . The highest concentrations among the calculated fractions characterised the undissolved, slowly biodegradable organic fraction (X_S). In raw wastewater, its concentration was between 408 and 837gO₂/m³. In raw wastewater, biodegradable fractions (S_S+X_S) constituted over 80% of total COD.

As a result of mechanical treatment wastewater in grit chamber, concentration of suspended solids, fractions X_I and X_S , were reduced average about 34 – 43% and the S_S fraction about 13%.

The determined percentage ratio of the individual fractions in raw wastewater dependent on the season is presented in Fig. 2. Among biodegradable fractions, fraction X_S which characterises slowly degradable suspensions and constitutes between 43.4 and 64.1 % of total COD is predominant. The ratio of fraction S_S (easily biodegradable organic contaminants) in total COD of the wastewater was between 24.0 and 38.0%. The percentage content of fraction X_I was at 4.4 – 18.1%. The lowest ratio, at 1.7 ÷ 3.4% in total COD of the tested raw wastewater, was that of fraction S_I .

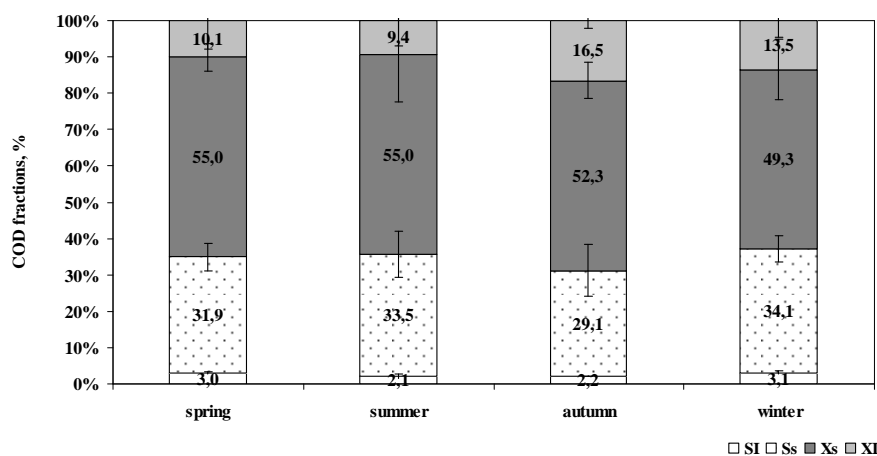


Fig. 2. The average percentage ratio of the individual fractions in total COD of raw wastewater in different seasons

Changes in the percentage of COD fractions in wastewater after grit chamber dependent on the season are shown in Fig. 3. The data show that in the wastewater after grit chamber percentage of S_S fraction was higher than in raw wastewater and ranged from 34.2 to 53.0%.

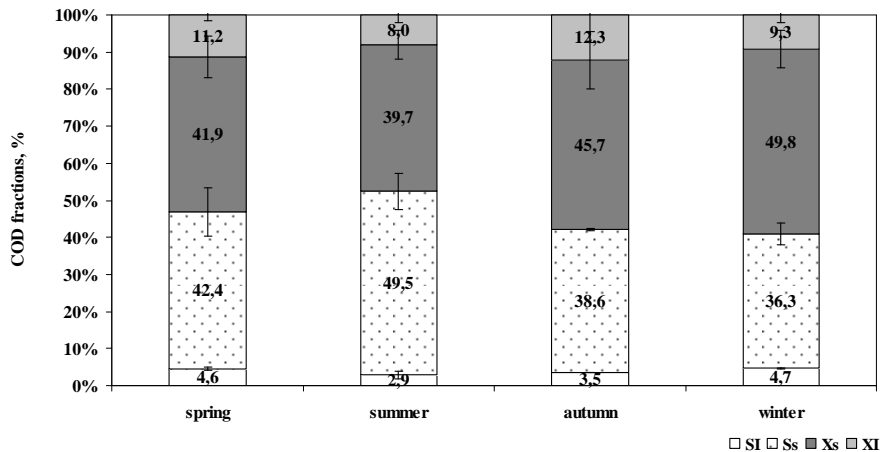


Fig. 3. The average percentage ratio of the individual fractions in total COD of wastewater after grit chamber in different seasons

The other hand the percentage of particulate slowly biodegradable substrates – fraction X_S was lower than in raw wastewater and ranged from 36.9 to 53.3%. In the wastewater after grit chamber biodegradable fractions (S_S+X_S) constituted still over 80% of total COD.

6. DISCUSSION AND CONCLUSIONS

The test results with the average percentage ratios of the individual fractions in raw wastewater and in wastewater after grit chamber are presented in Fig. 4.

Both in raw wastewater and in wastewater after grit chamber, over 80% of total COD constituted biodegradable fractions (X_S+S_S). The presented results show that in raw municipal wastewater the average percentage ratio of the individual COD fractions was as follows: $X_S=52.9\pm 6.7\%$, $S_S=32.2\pm 4.6\%$, $X_I=12.4\pm 5.3\%$ and $S_I=2.6\pm 0.6\%$, while in the wastewater treated in grit chamber was respectively: $X_S=44.2\pm 6.0\%$, $S_S=41.7\pm 6.3\%$, $X_I=10.2\pm 3.5\%$ and $S_I=3.9\pm 0.9\%$.

The study found that, the percentage ratios of X_S and X_I fractions in the wastewater after grit chamber relative to the value in raw wastewater has decreased, while the percentage ratios of S_S and S_I fractions has increased. The obtained results may indicate of the hydrolysis of suspended solids fraction already in the mechanical part of the plant. This is confirmed by the reduction in

the mechanical treatment the percentage of X_S fraction with a parallel increase in the percentage of S_S fraction. This changes are particularly evident in the spring and summer.

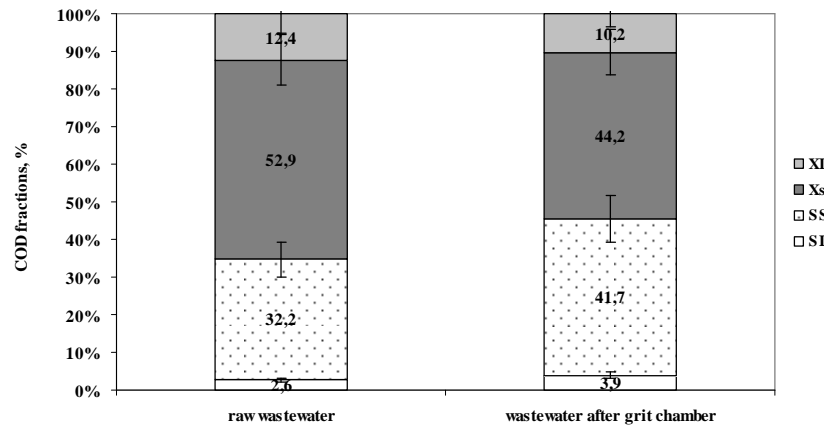


Fig. 4. The average percentage ratio of the individual fractions in total COD of raw wastewater and of wastewater after grit chamber

The research has shown that the fraction occurring in the highest concentration in raw wastewater is X_S , followed by S_S , X_I and S_I . Such an order is present in the biokinetic models (Tab. 3). Significant differences between actual research and model assumptions 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 assumptions of the ASM1 and ASM2 models, and lower percentage ratios of fractions S_I and X_S in the raw wastewater.

Table 3. The percentage COD fraction ratio in raw wastewater according to own research and the assumptions of the ASM1 and ASM2 models

| COD fractions,% | WWTP with the output >40 000 P.E. | in ASM1 model | in ASM2 model |
|-----------------|-----------------------------------|---------------|---------------|
| | raw wastewater | | |
| S_I | 1.7 – 3.4 | 5.0 | 5.0 – 10.0 |
| S_S | 24.0 – 38.0 | 15.0 | 12.0 – 30.0 |
| X_I | 4.4 – 18.1 | 10.0 | 10.0 – 15.0 |
| X_S | 43.4 – 64.1 | 70.0 | 35.0 – 75.0 |

The presented test results are a basis for the formulation of final conclusions:

The concentrations and percentage ratios of the individual COD fractions in raw wastewater determined in real conditions differ from the values assumed by the ASM models. The real concentrations and percentage ratios of the individual COD fractions in raw wastewater should be a basis for the calibration

of models used in the modelling and control of the operation of wastewater treatment plants.

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FRAKCJE CHZT W ŚCIEKACH SUROWYCH I MECHANICZNIE OCZYSZCZONYCH

Streszczenie

W artykule przedstawiono wyniki badań dotyczące frakcji ChZT w ściekach surowych i mechanicznie oczyszczonych w piaskowniku. Badania prowadzono w mechaniczno-biologicznej oczyszczalni ścieków o wielkości >40 000 RLM, zlokalizowanej w zachodniej Polsce. Próbkę do badań pobierano w różnych porach roku. Metodyka wyznaczania frakcji ChZT została opracowana w oparciu o wytyczne ATV-131. Podczas badań określono następujące frakcje: substancje organiczne w zawiesinie, biologicznie wolno rozkładalne (X_S), rozpuszczone substancje organiczne, biologicznie łatwo rozkładalne, (S_S), substancje organiczne w zawiesinie, biologicznie trudno rozkładalne (X_I) i rozpuszczone substancje organiczne, biologicznie nierozkładalne (S_I). Rozdziału frakcji rozpuszczonych i w zawiesinie dokonano przez filtrację próbek ścieków przez filtry membranowe o wielkości porów 0,45 μm . Wyniki badań wykazały, że zarówno w ściekach surowych jak i oczyszczonych mechanicznie udział frakcji biodegradowalnych wynosił ok. 80% całkowitego ChZT. Oczyszczanie ścieków w piaskowniku spowodowało obniżenie stężenia zanieczyszczeń ograniczonych o ok. 30% oraz wpływało na zmiany w udziale frakcji rozpuszczonych i w zawiesinie. Wartości procentowego udziału frakcji X_S i X_I w ściekach po piaskowniku zmalały, podczas gdy wartości procentowego udziału frakcji S_S i S_I wzrosły, w stosunku do ich udziału w ściekach surowych. Udział procentowy frakcji ChZT w ściekach surowych wyznaczony w badaniach różni się od danych zawartych w modelach ASM1 i ASM 2.

