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COD FRACTIONS IN MUNICIPAL SEWAGE - COMPARISON OF DETERMINATION METHODS

Summary

The thesis presents an overview and characteristics of three different methods for determining the fraction of organic compounds in sewage: methods according to ATV guidelines, respirometric methods and particle separation methods. The results of laboratory analyses of sewage composition carried out with each of the described methods are presented. The sewage came from the sewerage collector in Grodzisk Wlkp. The research was carried out in 7 series, from October 2013 to May 2014. The results obtained with different methods were compared using a statistical test. Differences are a consequence of conventionally accepted coefficients and ranges of particle size and errors during the manual separation of particles

Key words: municipal sewage, organic impurity fractions, methods for determining organic impurities fraction

INTRODUCTION

The content of organic compounds in sewage is usually determined as a five-day biochemical oxygen demand (BOD_5) or chemical oxygen demand (COD). The average values of these indicators are respectively 430 and 860 mgO_2/dm^3 [Miksch and Sikora 2010]. In mathematical models used to simulate biological sewage treatment, such as widely used models from the ASM group, organic compounds are expressed as COD [Rössle and Pretorius 2001, Pasztor et al. 2009, Wu et al. 2014], in contrast to the models from the ASAL group based on the BOD balance [Sochacki et al. 2009, Stokes et al. 2000]. This indicator is usually designated as COD total; it then covers the whole group of compounds, in various

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forms and decomposing at different rates. The course of individual unit processes, such as nitrification, denitrification or dephosphatation, however, depends on the type of organic compounds in the treated sewage. For this reason, the fractions of organic compounds are distinguished, dividing them into dissolved and undissolved as well as easily, hardly and non-decomposable (inert).

Determination of the fraction of organic compounds contained in sewage can be carried out by various methods [Baczyński 2010] based on different criteria. Physical and chemical methods rely on the separation of organic particles contained in sewage by means of filtration, centrifugation or coagulation and COD determination in individual fractions. Respiratory methods are based on measuring the amount and rate of oxygen or nitrate consumption in biological processes and allow for more precise characterization of the COD degradable fractions. The literature gives numerous examples in this regard [Baczyński 2010, Myszograj 2008, Myszograj i Sadecka 2004, Struk-Sokołowska 2014, Zawilski and Brzezińska 2009].

Due to the assumptions and the method of making the determinations and the related problems, the results obtained for the same sewage may be different. For this reason, the objective of the thesis is to determine the fraction of organic pollutants in domestic sewage by various methods, compare the results obtained and assess the accuracy of the methods used.

FRACTIONS OF ORGANIC COMPOUNDS

The division into organic compound fractions contained in sewage is basically conventional. The percentage of individual fractions in the total COD given in Figure 1 is approximate and depends on the source of sewage, the time of flow through the sewage system and the purification stage. Individual fractions undergo various changes during purification processes, and their participation in the organic substrate affects individual processes.

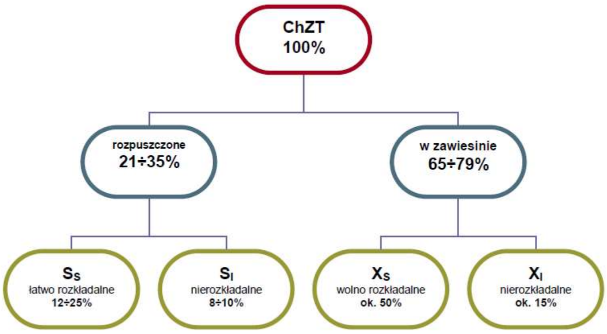


Fig. 1. Division of organic compounds into fractions [Sadecka et al. 2011]

The easily decomposable dissolved fraction can be directly absorbed by microorganisms and provide them with a source of energy, which makes it perform an important task in the processes of denitrification and dephosphatation. The non-decomposable (inert) dissolved fraction does not undergo any changes during the purification process. The slowly decomposable suspended fraction may be retained on biomass particles and removed with them from the purification system or be hydrolysed to dissolved compounds and only then can be used by microorganisms. The non-decomposable suspended fraction can only be removed together with the biomass, where its amount above 0.15 COD can cause problems for the active biomass. The total COD can therefore be recorded as the sum of the above-mentioned components [Makowska and Spychała 2014].

$$ChZT_{całk.} = S_S + S_I + X_S + X_I (1)$$

where:
COD_{total} - value of total chemical oxygen demand, mgO_2/dm^3,
S_S - easily decomposable dissolved fraction, mgO_2/dm^3,
S_I - biologically non-decomposable dissolved fraction, mgO_2/dm^3,
X_S - biologically slowly decomposable suspended fraction, MgO_2/dm^3,
X_I - biologically non-decomposable suspended fraction, mgO_2/dm^3.

The basic indicator of the content of the easily decomposable organic substrate is biochemical oxygen demand, understood as oxygen consumption in biochemical processes over time, usually determined as a five-day oxygen demand (BOD_5). The course of biochemical oxidation depends on the amount and activity of microorganisms, temperature and pH of sewage and the content of toxic substances [Myszograj 2005].

$$BZT_t = BZT_{całk.} * \left(1 - e^{-k*t}\right)(2)$$

where:
BOD_t - BOD value for incubation time t, mgO_2/dm^3,
BOD_{total} – total oxygen demand for the first decomposition phase, mgO_2/dm^3,
k - reaction rate constant, d^{-1}.

The above equation is used to determine the BOD_{total} and the reaction rate constant k.

Most of the methods used to determine the fraction of organic compounds use the measurement of oxygen uptake rate in the form of BOD or OUR. In practice, the most common method is the determination of organic fractions according to ATV guidelines [Makowska and Spychała 2014, Myszograj 2005]. It is based on the determination of COD of dissolved organic substances and total BOD and the

rate of decomposition of organic substances. The ISO 15705:2002 standard is also used for this purpose [Borg and Ekström 2015]. For the determination of easily decomposable substances, the OECD 301F test may also be used, in which the amount of oxygen uptaken over 28 days is compared to the amount of oxygen needed for complete degradation of the substrate. The COD value of decomposition fractions is determined on the basis of total BOD [Myszograj 2008].
Accurate determination of the easily decomposed dissolved fraction S_S allows a respirometric method to measure the rate of oxygen consumption *(Oxygen Uptake Rate* - OUR). The measurement can be carried out in a laboratory reactor with activated sludge, flow or batch method (in the variant of high or low biomass load). An important element is the correct adoption of the heterotrophic growth rate for the experimental conditions [Ekama et al. 1986]. The calculation of fraction size is carried out on the basis of the graph. An exemplary graph of oxygen consumption rates is shown in Figure 2.

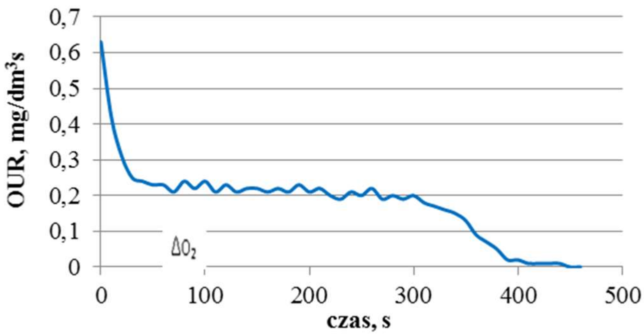


Fig. 2. An example of a curve of oxygen uptake rate in the respirometric method

COD fractions can also be determined by dividing the organic matter by particle size [Czerwionka and Mąkinia 2009]. The basis of the analysis is the division of particles as in the figure. 3.

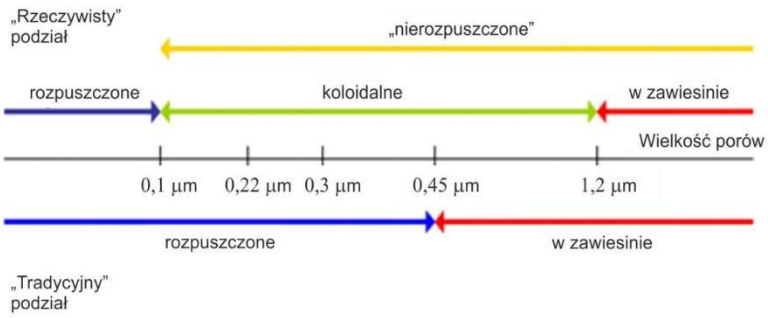


Fig. 3. Fractionation of organic carbon depending on the pore size of the filters; real and traditional division [Czerwionka et al. 2009]

According to the above source, the "real" division takes into account the content of dissolved and colloidal and suspended fractions, which make up the undissolved fraction; division limits are particle diameters of 0.1μm and 1.2μm. The "traditional" division includes two groups of compounds: dissolved and contained in the suspension; the division limit is 0.45 μm diameter.

The studies of particle size in sewage and their relationship with COD were conducted by many authors [Hocaoglu and Orhon 2013, Baczyński 2010].

RESEARCH METHODOLOGY

Sewage for testing came from a sanitary sewage system located in a small town. Samples were collected seven times in half a year, from October to March, with the help of a telescopic bucket from a sewage well on the section supplying domestic sewage from a place inhabited by about 800 people directly to the treatment plant. Laboratory studies involving the determination of COD (by the dichromate method in an acidic environment) and BOD_5 (respirometric method) were carried out the same day in the analytical laboratory of the Department of Water and Sanitary Engineering. Fractions of organic pollutants contained in sewage were determined by three methods: according to ATV guidelines, according to particle size and respirometric method.

<u>The method according to ATV-131 guidelines</u>

The size of the biologically non-decomposable fraction S_I was calculated as 5% of the value of S_{COD}:

$$S_I = 0{,}05 * S_{ChZT} \quad (3)$$

where:
S_{ChZT} – suma rozpuszczonych substancji organicznych, mgO_2/dm^3.

The COD of dissolved organic substances was determined in a sample filtered using the standard method (potassium dichromate in an acidic environment with silver sulphate as a catalyst, reading in a photometer in visible light).

The size of the easily decomposable fraction S_S was calculated as the difference between S_{COD} and S_I:

$$S_S = S_{ChZT} - S_I \quad (4)$$

The size of the suspended fraction of slowly decomposable X_S was determined as the BOD_{total} difference (including inertial fraction) and the dissolved fraction of easily decomposable S_S:

$$X_S = \frac{BZT_{całk}}{1-f_{BZT}} - S_S (5)$$

where:
f_{BOD} - factor including inertial fraction, -; $f_{BOD} = 0.15$ was assumed whereby the total biochemical oxygen demand for the first decomposition phase together with the rate constant k was determined using the Polymath program.

The concentration of fraction X_I was determined from the equation:

$$X_I = X_S / (1 - A) - X_S (6)$$

where:
A - factor depending on the type of sewage, $-$ (according to ATV A = 0.25)

The total concentration of fraction X_{COD} is the sum of suspended, decomposable and non-degradable fractions:

$$X_{ChZ} = X_S + X_I (7)$$

where:
$X_S -$ suspended decomposable fraction of COD, mgO_2/dm^3 ,
$X_I -$ suspended biologically non-decomposable fraction of COD, mgO_2/dm^3.

Particle separation method

Determination of fractions method of particle separation was carried out similarly as in the cited work by Czerwionka and Mąkinia [2009]. Syringe filters were used to separate the particles. Due to the different sizes of colloidal particles given in the literature [Bodzek 2011, Łomotowski and Szpindor 1999], the sewage was filtered successively through filters with 1.0 and 0.2 µm pore diameter, and the COD value was determined in three samples: in non-filtered (C_0), after filtration through a filter with a larger pore diameter (C_1) and after filtration through a filter having a smaller pore diameter (C_2). The dissolved fraction is directly the C_2 value, the colloidal fraction is the C_1 - C_2 difference, the suspended fraction is C_0 - C_1, and the undissolved fraction being the sum of suspended and colloidal particles is the C_0 - C_2 difference.

Respiratory method

The respirometric method uses the measurement of OUR oxygen uptake rate carried out in a container with activated sludge, with a low biomass load of BOD_5 [Ekama et al. 1986]. An oxygen sensor and multifunctional CX-742 meter with automatic temperature compensation were used. The curve in the OUR = f (t) system was drawn, and the content of the easily soluble fraction S_S was calculated according to the equation:

$$S_{S}=\Delta O_2 \cdot \frac{1}{1-Y_H} \cdot \frac{V_{os}+V_{ś}}{V_{ś}} \quad (8)$$

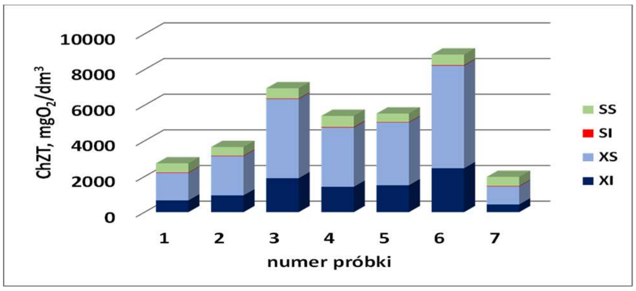
where:
ΔO_2 - unit change in oxygen concentration in sewage (calculated on the basis of the area under the curve), mgO_2/dm^3s,
V_{os} - volume of sludge used, dm^3,
$V_{ś}$ - volume of sewage used, dm^3,
Y_H - growth factor of heterotrophs under aerobic conditions, 1/s.

The sizes of the other fractions were calculated as per the ATV-131 method (equ. 5 – 7).

RESEARCH RESULTS AND DISCUSSION

The following figures show the results of fractionation of organic pollutants made by the methods described above. Figure 4 shows the content of the fraction expressed as COD. The values obtained by ATV and respirometric methods are similar, whereas larger differences were found between the results obtained by these methods and the values obtained by particle separation (especially for the X_i and $X_s$suspended fractions). In the results of the respirometric method, due to the failure of the measuring apparatus, the sample No. 4 was omitted.

a)



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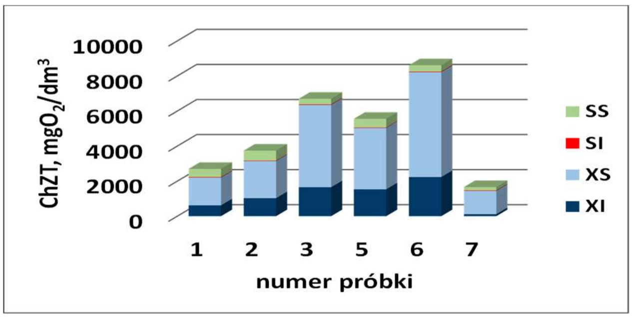

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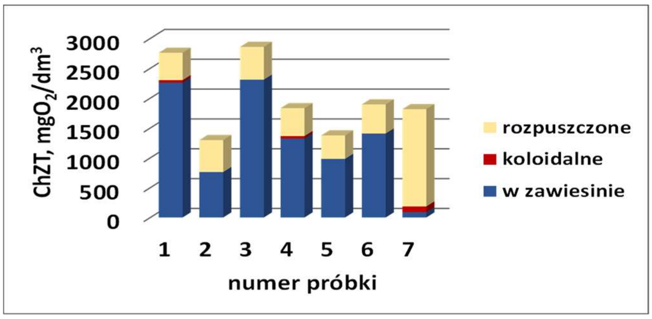
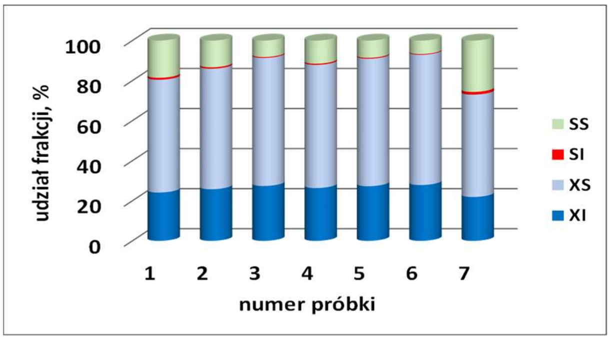


Fig. 4. COD fractions determined by the method: a - according to ATV-131, b - respirometric, c - particle separation

Large differences between the COD values from individual measurements result from the high variability of the composition of sewage from a small sewage system. Differences between the results obtained by different methods, especially between respirometric methods and the particle separation method, result from the lower accuracy of the latter.

Similarly, there is a comparison between the methods used for the percentage of individual fractions. The results obtained from the particle separation method differ markedly from the others (Fig. 5).

a)



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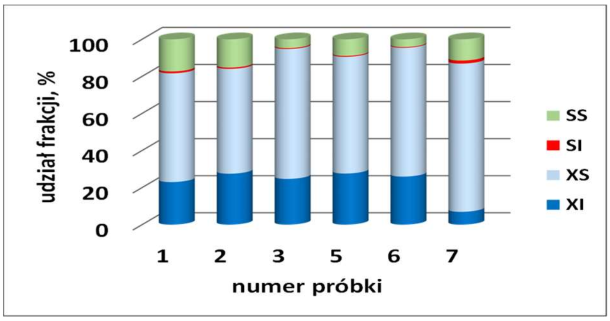

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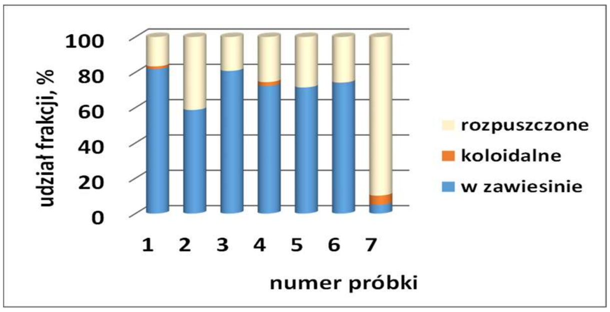
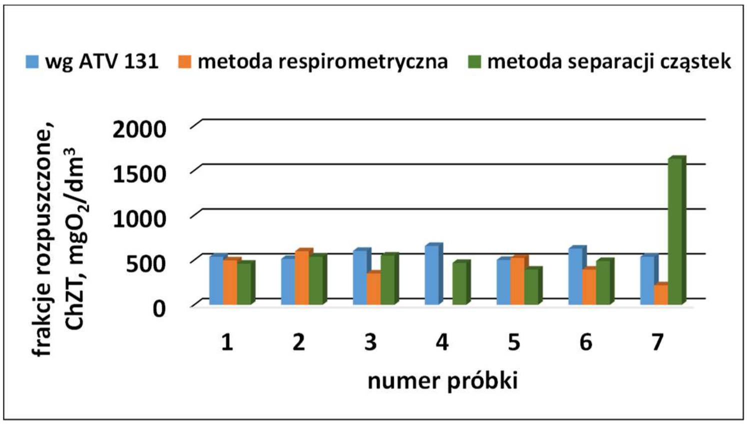


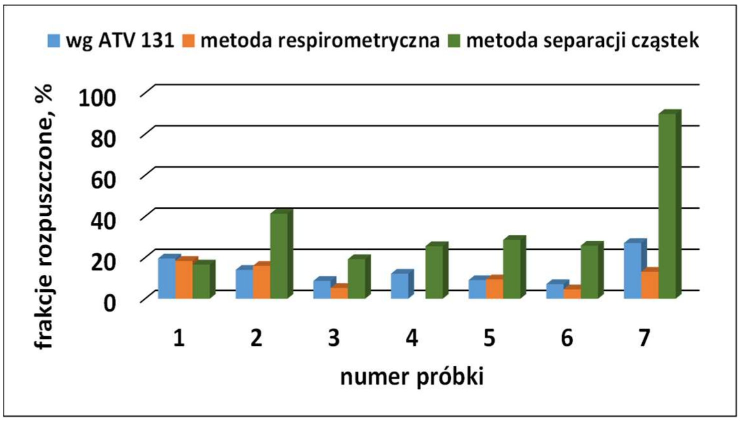
Fig. 5. Percentage of organic fraction in sewage calculated on the basis of values determined by the method: a - according to ATV-131, b – respirometric, c - separation of particles

The obtained values, for example in terms of the dominant fraction of Xs are comparable with literature data - 35-77% in a combination of data from various sources presented by Borg and Ekström [2015] and 34-62% in the values compiled by Szaja et al. [2014]. The total COD obtained by particle separation is, in turn, considerably greater than that given by Czerwionka and Mąkinia [2009] due to the high content of suspended particles in the treated sewage from the sewerage channel in which relatively small sewage flow rates were observed (from 0.16 up to 0.25 m/s).

Another analysis of the results was carried out after the division of the fraction into dissolved and suspended (analogous to the so-called "real" division). The content of dissolved ΣS ($S_I + S_S$) and suspended ΣX ($X_I + X_S$) fractions expressed as COD and the percentage fraction dissolved and suspended in total COD was compared (Fig. 6).

a)





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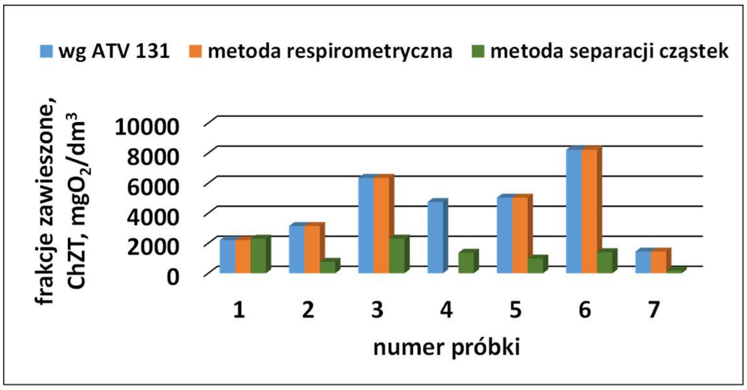

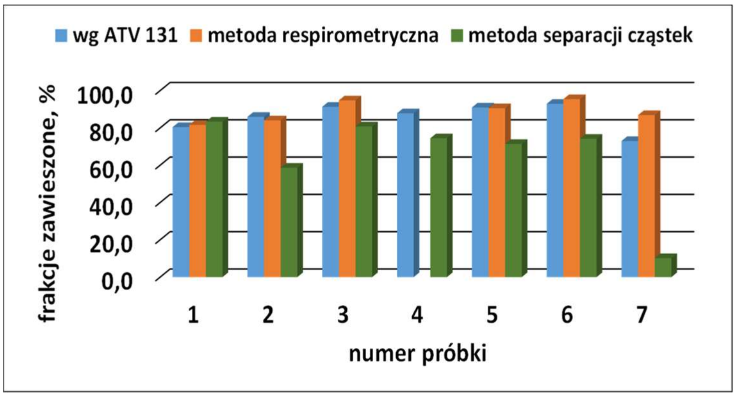

Fig. 6. Content of suspended and dissolved fractions in the tested sewage, determined by various methods; a - dissolved fractions, b - suspended fractions

Higher agreement between the results obtained with different methods was found for the method according to the ATV guidelines and the respirometric method, with larger differences found in the case of suspended fractions.

The above considerations were confirmed by statistical analysis carried out with the t-Student test (Table 1).

Tab. 1. Results of statistical analysis of results; "Yes" - significant difference in average, "no" - no significant difference in average

Dissolved fractions	METHOD		
ΣS	ATV	Particle separation	Respirometric
ATV	X	No	No
Particle separation	No	X	No
Respirometric	No	No	X

Dissolved fractions	METHOD		
ΣS	ATV	Particle separation	Respirometric
ATV	X	YES	No
Particle separation	YES	X	YES
Respirometric	No	YES	X

CONCLUSIONS

Fractionation of the organic substrate contained in the sewage can be carried out by various methods. However, it should be remembered that each of them is burdened with errors resulting from the adopted assumptions (e.g. coefficients *A* and f_{BZT5} in the ATV method) and related to the analysis (e.g. the method of sample filtration by microsamples in the particle separation method). The sewage susceptibility to biochemical degradation and the character of suspended particles depend to a large extent on the source of sewage, including the lifespan of sewage system users, the amount of washing and washing agents used, and water consumption. Fractionation by particle size should take place to a much greater extent, with the help of image analysis methods; for individual sources, a separate analysis of grey and black sewage is recommended. Sewage filtration through microparticles should be done at set parameters, which would allow partial elimination of accidental error. Differences that have been obtained between the content of organic fractions obtained by various methods result from the methodological imperfections outlined above. Nevertheless, such analysis of sewage composition allows to obtain information on their susceptibility to biochemical degradation and is helpful in the selection of methods for purification and operation of devices, whereas differences between the results obtained in the work and literature data [Sadecka 2010, Sadecka et al. 2011] are caused by the different origin of the material used in the research.

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