Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25629

186 (2020) 443–449
May

COD and nitrogen compounds balance in mechanical-biological wastewater treatment plant with sludge treatment

Sylwia Myszograj*, Ewelina Płuciennik-Koropczuk

University of Zielona Gora, Faculty of Civil Engineering, Architecture and Environmental Engineering; Institute of Environmental Engineering Szafrana St.15, 65-246 Zielona Góra, Poland, emails: S.Myszograj@iis.uz.zgora.pl (S. Myszograj), E.Pluciennik@iis.uz.zgora.pl (E. Płuciennik-Koropczuk)

Received 4 December 2019; Accepted 5 February 2020

ABSTRACT

The article describes the methodology for balancing organic carbon and nitrogen compounds with the use of chemical oxygen demand (COD) fractionation. Calculations were made for the technological system of mechanical and biological wastewater treatment (PE 22 735) with anaerobic/anoxic/oxygen bioreactor and processing of sewage sludge. A high average degree of pollution removal were respectively: biochemical oxygen demand – 97%, COD – 93%, suspensions – 91% and 83% for nitrogen compounds. In raw wastewater, 78% of total COD were biodegradable organic compounds, and about 93% of total nitrogen was ammonium nitrogen. It was found that the processes of mechanical wastewater treatment have an impact on the share of organic substances in the sewage flowing into the biological part. The sieves remove a significant portion of the slowly biodegradable suspension. Despite different fractions of individual fractions in raw wastewater, treated wastewater was characterized by comparable parameters, respectively: for COD, non-biodegradable fractions constituted 88%, and for total nitrogen: 55% – $N–NO_3$, 33% – $N–NH_4$, 12% – organic nitrogen, respectively. The results obtained and the balance sheet prepared confirmed the so-called "COD loss" theory, according to which close 100% COD balance simulations are only possible for oxygen reactors or anoxic/oxygen systems.

Keywords: Pollution balance; COD fractionation; Nitrogen compounds

1. Introduction

One of the directions of water protection is protection against pollution coming from insufficiently treated wastewater. By joining the European Union, Poland undertook to comply with the requirements of Council Directive 91/271/EEC of May 21, 1991 regarding urban wastewater treatment (Official Journal EC L 135 of 30.05.1991) following the transition dates and periods specified in the negotiations and stipulated in the Accession Treaty. According to the directive, the entire area of Poland, due to the overall location in the Baltic Sea catchment, was considered the so-called sensitive area, which requires a significant reduction of discharges of nitrogen and phosphorus compounds and biodegradable pollutants into waters. Important assumptions of the directive are: ensuring wastewater treatment with an increased standard of nutrient removal in agglomerations above 10,000 PE and ensuring a 75% reduction of the nitrogen and phosphorus load about the load flowing into the treatment plant. Therefore, it is understandable to strive for conducting biological wastewater treatment in a way that ensures maximum reduction of nitrogen and phosphorus compounds in the wastewater.

Characteristics of nitrogen compounds in raw wastewater are most often based on the analysis of total/general Kjeldahl nitrogen (TKN = organic nitrogen + ammonium nitrogen). The share of both forms depends on the time of wastewater retention in the sewage network because it is where the hydrolysis of organic nitrogen to ammonium begins. Nitrate

* Corresponding author.

Presented at the 14th Conference on Microcontaminants in Human Environment, 4–6 September 2019, Czestochowa, Poland

1944-3994/1944-3986

and nitrite nitrogen content are usually not included. For more accurate wastewater characteristics, it is assumed that nitrogen occurs in the forms [1]:

$$N_{tot} = S_{N-NO_2^-} + S_{N-NO_3^-} + TKN = S_{N-NO_2^-} + S_{N-NO_3^-} + S_{N-NH_4^+} + S_{I,N} + X_{S,N} + X_{I,N}, gNm^{-3} \tag{1}$$

where $S_{N-NO_2^-}, S_{N-NO_3^-}$ – nitrite and nitrate–nitrogen concentration, gNm^{-3}; TKN – total nitrogen concentration as determined by the Kjeldahl method (ammonium and organic nitrogen), gNm^{-3}; $S_{NH_4^+}$ – ammonium nitrogen concentration (ammonium ion and undissociated ammonia), gNm^{-3}; $S_{I,N}$ – concentration of dissolved organic nitrogen contained in non-biodegradable compounds, gNm^{-3}; $X_{I,N}$ – concentration of the non-bioavailable organic nitrogen contained in the total suspension, gNm^{-3}; $X_{S,N}$ – concentration of easily bioavailable organic nitrogen in the total suspension, gNm^{-3}.

In the process of wastewater treatment, ammonification is continued, the product of which ammonium nitrogen can be assimilated, that is, used to build a bacterial mass or oxidized in the nitrification process to nitrite (III) and nitrate (V). The mentioned processes (ammonification, nitrification) do not cause changes in the total nitrogen concentration in wastewater, but a change in the forms of nitrogen occurrence appears. All microorganisms participating in biological wastewater treatment processes need nitrogen to grow. They use it most often in the form of organic and ammonium nitrogen and its absence use nitrates. With the adopted stoichiometric formula for biomass $C_5H_7NO_2$, nitrogen constitutes about 12.3% of its mass. Another process - denitrification causes the reduction of nitrite (III) or nitrate (V) nitrogen to free gaseous nitrogen, thus contributing to the permanent removal of total nitrogen from wastewater. It should also be noted that a significant amount of nitrogen remains assimilated in biomass and is removed with excess sludge for processing. The importance of liquids arising in the processes of thickening, dewatering or biological treatment of sewage sludge is underestimated due to their small amount and insignificant share in the total amount of treated wastewater. However, a large load of impurities contained in sludge liquids can pose a threat to the proper functioning of the treatment plant. The literature gives divergent values of pollutant loads recycled with sludge liquids to the wastewater treatment system [2]. Sludge liquids are most often characterized by a high content of organic compounds and biogenic compounds, in particular ammonium nitrogen and phosphates, general suspension, usually hardly falling colloidal, the content of fats and heavy metals [3].

The main problem in optimizing the activated sludge method in mathematical models is the lack of a parameter that clearly defines the share of organic mass in wastewater and activated sludge biomass. Knowledge of the organic carbon content in wastewater allows to design an appropriate method of its removal and effectively reduce other pollutants, primarily nitrogen and phosphorus removal. It also gives the possibility to optimize individual unit processes, and above all to monitor processes occurring in the activated sludge chamber [4]. Also, organic carbon is an important indicator when assessing the content of organic substances in wastewater sludge. This makes it possible to determine the susceptibility of sludge decomposition and the selection of an appropriate method of management. Most often, specific quality indicators of the substrate, such as COD, BOD_5, total organic carbon or dry organic matter (DOM) are used to assess the share of organic substances [5]. COD and DOM are a measure of the total amount of organic matter, and BOD_5 is most often described as the biodegradable part of organic compounds. In many cases, such, rather general information about the organic matter contained in the wastewater is insufficient, which necessitates more accurate characteristics. Detailed characteristics of organic substances in wastewater can be achieved by determining the COD fraction (Fig. 1).

COD fractionation of wastewater is widely used in modeling biochemical processes occurring in the process of wastewater treatment with activated sludge and anaerobic processes.

Preparation of the COD balance requires comprehensive information on, among others [7–10]:

- technological data (amount of wastewater, the volume of bioreactors, recirculation rate, sludge management, etc.);
- changes in COD and concentration of nitrogen compounds bioreactors;
- DOM dry organic matter content and determination of the COD quotient in activated sludge.

The basis for preparing the balance is the determination of the COD load supplied to the activated sludge chambers and the COD load discharged with treated wastewater and taking into account such components as:

- COD charge oxidized in the biological wastewater treatment process (quantitatively described by the number of electrons disconnected from organic substrates (dehydrogenation) and attached to the acceptor);
- COD charge contained in organic particles adsorbed on activated sludge flocs and assimilated by activated sludge biomass during cell synthesis and then discharged with excessive sludge.

The study aimed to prepare a balance of nitrogen and COD compounds during the technological process of sewage treatment plants based on laboratory tests.

2. Methodology of the study

2.1. Research object

The tests were carried out in a mechanical-biological sewage treatment plant with an operational capacity of 6,450 $m^3 d^{-1}$ (22 735 PE) working based on the technology of low-loaded activated sludge in a circulation system. Wastewater from the city is fed via a pumping system to the wastewater treatment plant, and wastewater from the non-sewage area is transported with a slurry tanker and drained to a catchment point. Mechanical wastewater treatment occurs on sieves and an aerated grit chamber. Nitrification, denitrification, biological and chemical dephosphatation processes take place in the bioreactor. Partially stabilized excess sludge, from the secondary settler flows to the excess and recirculated sludge pumping station. From the pumping station, part of the sludge - recirculated sludge is recycled to the bioreactor, and excess sludge is pumped to the gravity thickener. Excessive sludge is dewatering in the press chamber. Dewatering precedes chemical preparation for the filtration process, that is, conditioning with iron salts and lime milk. The dewatering sludge is transferred to an enterprise dealing in the production of flower soil and garden fertilizers. The technological system of the analyzed wastewater treatment plant with marked localization of sampling points was presented in Fig. 2.

Samples of raw wastewater, sewage sludge and waste from subsequent technological objects were taken six times. In laboratory tests, the content of ammonia nitrogen, nitrate-nitrogen and total Kjeldahl nitrogen, total suspension, COD, BOD_5 was determined in filtered and non-filtered samples following the procedures in force at the accredited laboratory of the Institute of Environmental Engineering of the University of Zielona Góra, Poland.

The samples were given the following determinations: *W*1 – raw wastewater, *W*2 – wastewater after sieves, *W*3 – wastewater after grit, *W*4 – treated wastewater, *L*1, *L*2 – supernatant water from gravity thickener and liquids after dewatering, respectively, *S*1 – excessive sludge, *S*2 – sludge from gravity thickener, *S*3 – dewatered sludge

2.2. Methodology for determining the COD fraction

The methodology for determining the COD fraction has been included in the ATV-A131 guidelines [10]. Guideline ATV-DVWK A131P the dimensioning of single-stage sewage treatment plants with activated sludge, developed by the German Association of engineers and technicians of wastewater treatment, is widely used in design practice and at the stage of optimization and modeling of the wastewater treatment process. It allows us to describe processes based on wider than basic characteristics of raw wastewater. According to which, the determination of the S_S, S_I, X_S and X_I fraction is based on the determination of COD and BOD_5 in samples of filtered (0.45 μm) and unfiltered raw and treated wastewater, where:

- The COD of inert soluble organic substrates S_I is defined as COD in treated filtered wastewater.
- The COD of soluble readily biodegradable substrates S_S is calculated from the difference in the concentration of dissolved organic pollutants S_{COD} determined in raw filtered wastewater and fraction S_I:$S_S = S_{COD} - S_I$.
- The COD of particulate slowly biodegradable substrates X_S is defined as the difference of total BOD, calculated based on BOD_5 raw unfiltered wastewater and the rate of biochemical degradation and the easily decomposed dissolved fraction: $X_S = (BOD_5/k_1) - S_S$.
- The fraction of inert particulate organic substrates X_I is determined from the dependence: $X_I = X_{COD} - X_S$ where XCOD is the total COD of organic suspensions.
- The total COD of wastewater is the sum of all fractions: $T_{COD} = S_I + S_S + X_S + X_I$.

To determine the dissolved fraction, the method of filtering the wastewater samples through the 0.45 μm filter was assumed.

According to the methodology ATV-131, the value of fraction X_S is calculated based on the constant rate of biochemical degradation $k = 0.1$ d^{-1}, for which $BOD_{Tot} = BOD_5/0.6$. The calculation also assumes that the fraction S_I corresponds to the COD value is filtered treated wastewater. This assumption is reflected in the calculation of the S_S fraction because it is calculated based on the difference $S_{COD} - S_I$, which in treated wastewater is equal to zero in each case.

3. Results of the research and discussion

Quantitative and qualitative balance sheet in terms of COD and BOD_5 loads, total suspended solids and nitrogen in the analyzed technological system of the wastewater treatment plant is presented in Figs. 3 and 4, respectively. The volume of the separated screenings, sand and fats was considered exclusively in the quantitative balance sheet of the wastewater treatment plant.

The average values of the analyzed parameters in raw wastewater were respectively: COD – 554 g O_2m^{-3}, BOD_5 – 269 g O_2m^{-3}, total suspended solids – 263 gm^{-3}, ammonia nitrogen – 37 g Nm^{-3}, TKN – 40 g Nm^{-3}.

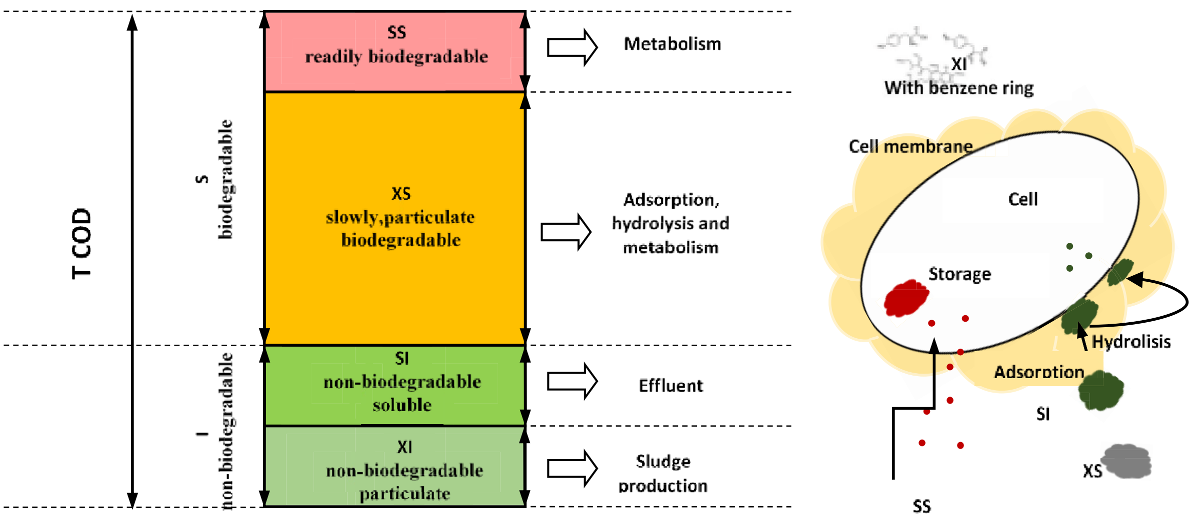

Fig. 1. Schematic diagram of the COD fractions and their fates in a biological wastewater treatment plant [6].

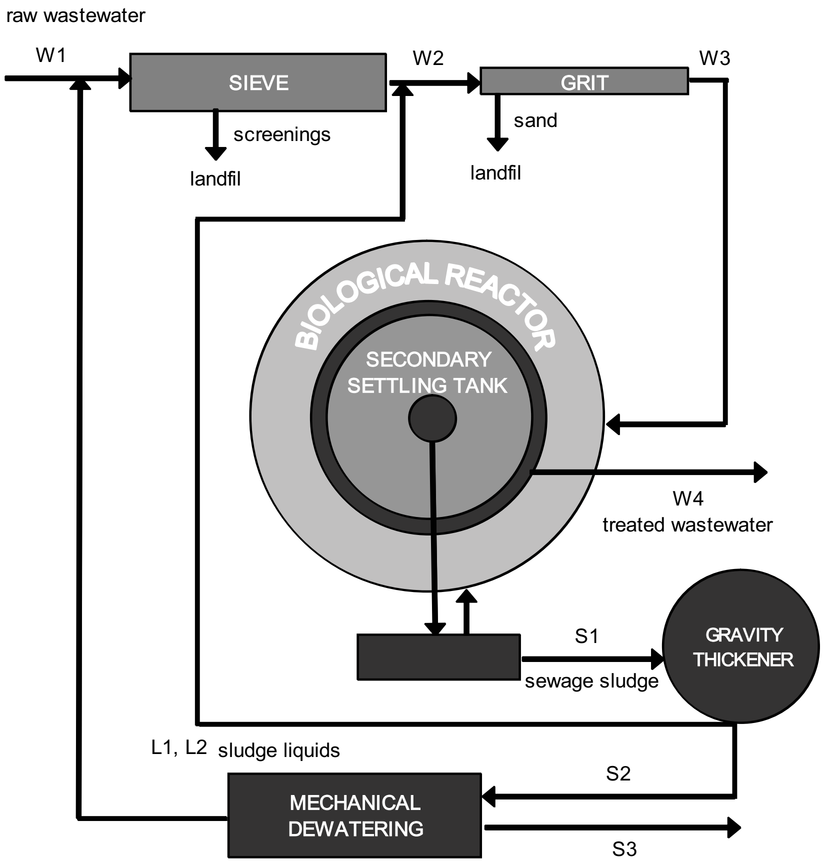

Fig. 2 Technological system of an analyzed wastewater treatment plant.

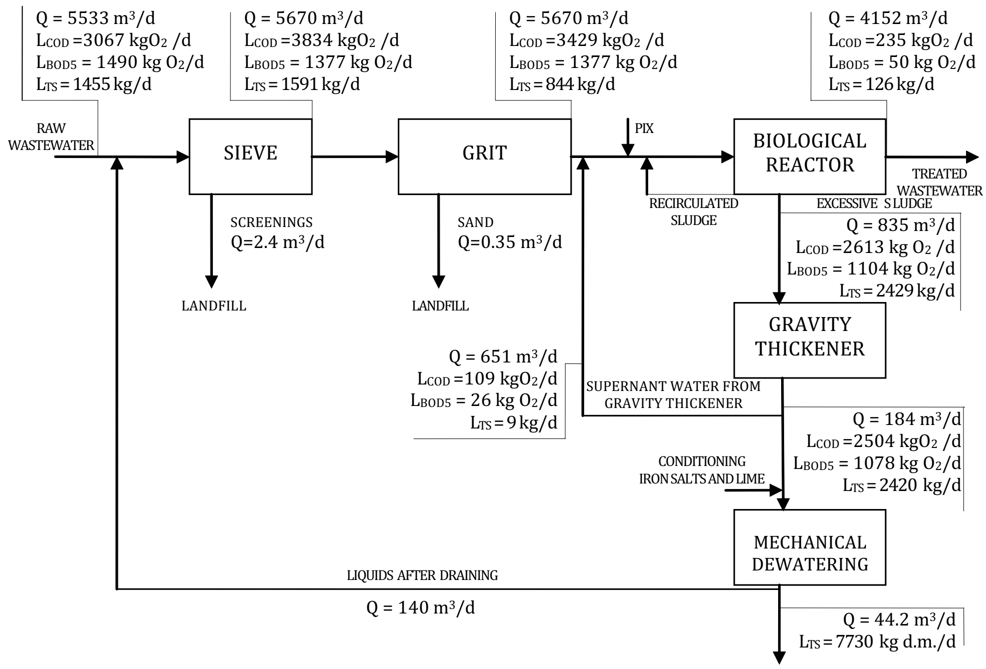

Fig. 3. Balance of COD, BOD, and TS load in a technological system.

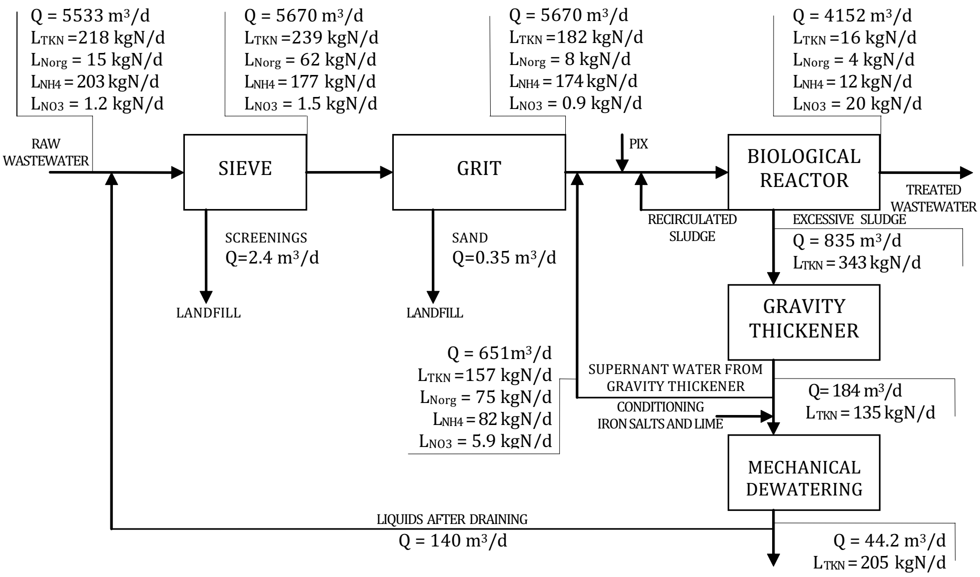

Fig. 4. Balance of TKN, organic (N_{org}), ammonium ($N–NH_4$), nitrate ($N–NO_3$) nitrogen load in the technological system.

As literature data proves, in the wastewater channeled to urban wastewater treatment plants nitrogen occurs mainly in the form of ammonium ion ($N–NH_4$) and inorganic compounds. Ratios between these forms of nitrogen are related to the source of wastewater. It was also proven that the time of delivery of wastewater to a wastewater treatment plant and conditions present in the sanitary sewage system has a significant impact on the value of this ratio, contributing to an increase in the proportion of ammonia nitrogen at the expense of organic nitrogen [11]. In the analyzed case the proportion of ammonia nitrogen in the raw wastewater was 92.5%, which indicates a highly advanced process of ammonification, which organic nitrogen undergoes in a complex sanitary sewer system that channels wastewater to the wastewater treatment plant, and a long period of channel retention.

Returning of leachates from the chamber filter press to the technological system through sieves caused an increase in pollution loads in the wastewater concerning the loads delivered with the raw wastewater to the wastewater treatment plant by respectively 25% of COD, 7.5% of BOD_5, 9.3% of total suspended solids and 9.6% of TKN. Supernatant waters from the gravitational densifier were channeled to the biological reactor and constituted additional pollution load with 3.5% of COD, 1.7% BOD_5, 1% of total suspended solids and 75% of TKN. Supernatant waters from the gravitational densifiers and leachates from mechanical dehydration of wastewater sediments, in comparison to post-fermentation liquids, are characterized by a lower concentration of pollutions, which are additionally decreased by the usage of polyelectrolytes for conditioning of sediments. Releasing of pollutions to supernatant waters in the gravitational densification process is strongly connected to the time of sediment densification [12]. Based on the data presented in literature it can be concluded that concentrations of ammonia nitrogen in this sort of leachate vary in a relatively wide range, and for the remaining pollution, indicators do not exceed 10%–15%. Therefore, in mechanically treatment wastewater channeled to bioreactors concentration of total nitrogen was still high and similar to the values marked in the raw wastewater (83% of load delivered with the raw wastewater) [13].

In the analyzed wastewater treatment plant a high degree of organic compounds removal was obtained, with: COD – 93% and BOD_5 – 97%, and also total suspended solids – 91%. Obtained results of total nitrogen removal were averagely 83%, which correspond with concentrations of total nitrogen in the treatment wastewater, 8.7 g Nm^{-3}, of which approximately 55% is nitric nitrogen and 33% ammonia nitrogen.

A load of COD discharged from the system was compared with a load of COD delivered with the raw wastewater, according to the Eq. (2):

$$\%COD = \left(\frac{LCOD_{out}}{LCOD_{in}}\right)\cdot 100 = \left(\frac{(2,613+235)}{3,067}\right)\cdot 100 = 93\% \qquad (2)$$

In the analyzed technological system of the wastewater treatment plant, a total load of COD corresponding with the consumption of organic compounds in the denitrification process and mineralization by heterotrophic bacteria, the load of COD discharged with the excessive sludge and the treatment wastewater was equivalent to a load of COD delivered to the biological section (balance 93%, in the balance sheet a load of COD discharged from the system along with screenings and sand, was not taken into account). Simultaneous conducting of processes in the biological reactor contributes to the treatment of wastewater without the creation of separate anaerobic zones, which would increase the uncontrolled loss of volatile organic compounds, which is then measured by the loss of COD, through mineralization of organic compounds [14]. The loss of COD indicated in the balance sheets results from the process of hydrolysis. Produced volatile fatty acids are mainly utilized by phosphoric bacteria in anaerobic conditions or simply lost during wastewater flow.

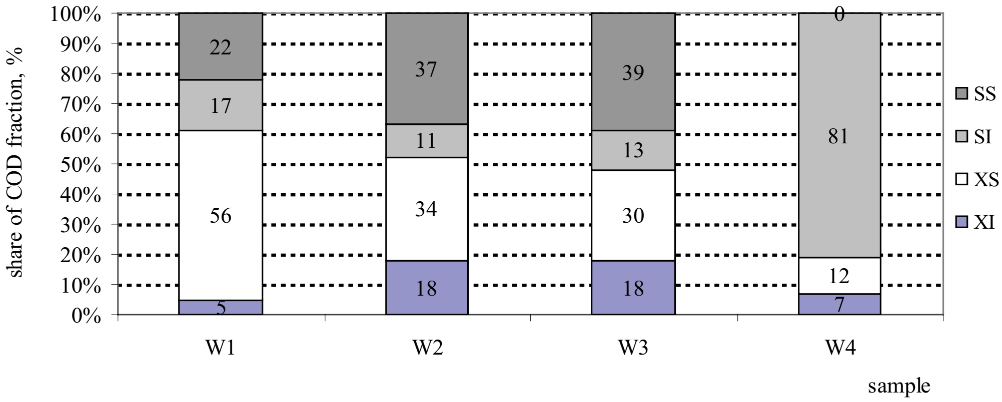

Fig. 5. Share of COD fraction in wastewater after subsequent technological objects.

Table 1
Proportion of COD fraction in urban raw wastewater

Frakcja	Kappeler and Gujer [15]	Sözen [16]	Płuciennik-Koropczuk and Myszograj [17]	Ekama [18]	Henze [19]	Ignatowicz [20]	Research results
	%						
S_S	10 – 20	9	50.0 – 61.7	20 – 25	24 – 32	33	22
S_I	7 – 11	4	2.2 – 6.0	8 – 10	8 – 11	7	17
X_S	53 – 60	77	22.0 – 34.4	60 – 65	43 – 49	44	56
X_I	7 – 15	10	8.0 – 16.2	5 – 7	11 – 20	16	5

In the raw wastewater averagely 78% of total COD was biodegradable organic compounds dissolved (S_S – 22%) and bound in suspended solid (X_S – 56%), which was determined during an analysis of COD fraction following the methodology ATV-A 131 (Fig. 5). Mechanically treated wastewater in the sieve-grit chamber system was characterized by an increase in the proportion of COD of dissolved substances. The proportion of suspension non-degradable fraction of COD, X_I increased from 5% in raw wastewater to 18% in mechanically treated wastewater. The proportion of this fraction in treated wastewater was approximately 7%. Such change is observed, because a load of COD in non-degradable suspended solid undergoes sorption on activated sludge and is to a large extent discharged with excessive sediment.

In the treated wastewater average COD values of the indicated fractions were: S_I = 45 gO_2m^{-3}, X_S = 8 gO_2m^{-3} and X_I = 4 gO_2m^{-3}, and the proportion in the total COD corresponding to them was as follows: S_I = 81%, X_S = 12% and X_I = 7%. Following the adopted methodology of estimating the COD fraction in treated wastewater no S_S fraction was recorded.

Table 1 presents the proportion of COD fraction in urban raw wastewater provided by various authors, and also the obtained results of research results.

The data set in Table 1 indicates that the proportion of COD fraction in urban wastewater is not constant and changes and the results obtained from the studies are comparable with those provided by other authors.

4. Conclusions

The mathematical description that is the basis for modeling wastewater treatment processes is based on theoretical knowledge and data from operated wastewater treatment plants, pilot installations, or laboratory tests. The basis for using the information obtained is their reliability, which can be confirmed by preparing mass balances of individual components. In practice, such balances are rarely prepared because of the need for detailed tests and measurements. It is often very difficult also for technical reasons. Undoubtedly, the basic and commonly used parameter characterizing organic substrates is COD.

The division of COD into fractions allows us to additionally assess the amount of non-biodegradable impurities and calculate the percentage of organic nitrogen fraction. However, the complexity of processes in anaerobic/anoxic/oxygen conditions causes problems with the determination of components that should be balanced. After subsequent technological structures for wastewater treatment, changes in the proportion of particular COD fractions and nitrogen compounds were reported, mainly resulting from the sieve filtering process and biochemical changes, for example, ammonification, nitrification and denitrification.

It was found that the processes of mechanical wastewater treatment have an impact on the proportion of dephosphatation processes organic substances in the sewage flowing into the biological section. The sieves remove a significant portion of the slowly biodegraded suspension material. The results obtained and the balance sheet prepared confirmed the so-called "COD loss" theory, according to which nearly 100% (93%) of COD balance simulations are only possible for anaerobic/anoxic/oxygen systems.

References

[1] S. Myszograj, The impact of temperature on the removal of nitrogen compounds in an activated sludge system, Curr. J. Appl. Sci. Technol., 11 (2015) 1–13.

[2] M. Włodarczyk-Makuła, PAHs balance in the solid and liquid phase of sewage sludge during fermentation process, J. Environ. Sci. Health, Part A, 43 (2008) 1602–1609.

[3] T. Ahmad Mohammad, M. Johari, M. Mohd Noor, A. Halim Ghazali, Assessment of using synthetic polymers in dewatering of sewage sludge, Desal. Water Treat., 57 (2016) 23308–23317.

[4] G.A. Ekama, M.C. Wenzel, Denitrification kinetics in biological N and P removal activated sludge systems treating municipal wastewater, Water Sci. Technol., 39 (1999) 69–77.

[5] A. Szaja, J.A. Aguilar, G. Łagód, Estimation of chemical oxygen demand fractions of municipal wastewater by respirometric method - case study, Annu. Set Environ. Prot., 17 (2015) 289–299.

[6] E. Płuciennik-Koropczuk, S. Myszograj, New approach in COD fractionation methods, Water, 11 (2019) 1484.

[7] A.M.E. Viana da Silva, R.J.N. Bettencourt da Silva, M. Filomena, G.F.C. Camões, Optimization of the determination of chemical oxygen demand in wastewaters, Anal. Chem. Acta, 699 (2011) 161–169.

[8] G.A. Baquero-Rodríguez, J.A. Lara-Borrero, J. Martelo, A simplified method for estimating chemical oxygen demand (COD) fractions, Water Pract. Technol., 11 (2016) 838–848.

[9] S. Myszograj, E. Płuciennik-Koropczuk, A. Jakubaszek, A. Świętek, COD fractions - methods of measurement and use in wastewater treatment technology, Civ. Environ. Eng. Rep., 24 (2017) 195–206.

[10] ATV-A 131-The Dimensioning of Single-Stage Sewage Treatment Plants with Activated Sludge, German ATV-DVWK Rules, and Standards, Hennef, German, 2000.

[11] J.P. van der Hoek, R. Duijff, O. Reinstra, Nitrogen recovery from wastewater: possibilities, competition with other resources and adaptation pathways, Sustainability, 10 (2018) 4605.

[12] M. Zahra, A. Abooalfazl, D. Mansooreh, Stabilization, and dewatering of wastewater treatment plants sludge using combined bio/Fenton-like oxidation process, Dry. Technol., 35 (2016) 545–552.

[13] S. Skinner, L. Dixon, D. Hillis, P. Rees, C. Wall, R. Cavalida, R. Usher, S. Stickland, A. Scales, Quantification of wastewater sludge dewatering, Water Res., 82 (2015) 2–13.

[14] M.C. Wentzel, G.A. Ekama, P.L. Dold, G. Marais, Biological excess phosphorus removal - steady-state process design., Water SA, 16 (1990) 29–48.

[15] J. Kappeler, W. Gujer, Estimation of kinetic parameters of heterotrophic biomass under aerobic conditions and characterization of wastewater for activated sludge modeling, Water Sci. Technol., 25 (1992) 125–139.

[16] S. Sözen, E.U. Çokgör, D. Ohron, M. Henze, Respirometric analysis of activated sludge behavior – II, Heterotrophic growth under aerobic and anoxic conditions, Water Res., 32 (1998) 476–488.

[17] E. Płuciennik-Koropczuk, A. Jakubaszek, A.S. Myszograj, S. Uszakiewicz, COD fractions in mechanical-biological wastewater treatment plant, Civ. Environ. Eng. Rep., 24 (2017) 207–217.

[18] G.A. Ekama, P.L. Dold, G.V.R. Marais, Procedures for determining influent COD, Fractions and the maximum species growth rate of heterotrophs in activated sludge systems, Water Sci. Technol., 18 (1986) 94 –114.

[19] M. Henze, Biological Wastewater Treatment: Principles Modeling and Design; M. Henze, M.C.M. van Loosdrecht, G.A. Ekama, D. Brdjanovic, Eds., IWA Publishing, London, UK, 2008.

[20] K. Ignatowicz, Analysis of COD fractions in raw wastewater flowing into small and large wastewater treatment plants, J. Ecol. Eng., 20 (2019) 197–201.