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*Original Research*

# Organic Compounds Fractionation for Domestic Wastewater Treatment Modeling

**Małgorzata Makowska*, Marcin Spychała****

Department of Hydraulic and Sanitary Engineering, Poznan University of Life Sciences,
Piątkowska 94A, 60-649 Poznań, Poland

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## Abstract

Organic compounds in domestic wastewater have a highly differentiated composition, which depends on the source of wastewater. Detailed fractionation of organic pollutants is indispensible to determine their transformation during treatment processes. Mathematical modeling requires the division of organic compounds in wastewater into the fractions: dissolved, suspended, biodegradable, and unbiodegradable. It is possible to determine the content of fractions based on $BOD_5$, COD, and reaction rate coefficients.

In this work, fractions of organic pollutants in wastewater, originating from small sources and treated in small treatment plants (0.66-22.00 $m^3$/d), were identified. For comparison, fractions of organic pollutants in a medium municipal wastewater treatment plant (WWTP) of 4,000 $m^3$/d capacity have been determined.

It was found that the wastewater from small sources and households differ in composition from typical municipal sewage. They are characterized by higher contents of dissolved and suspended biodegradable fractions. A similar result was found for septic tank effluent. The high content of biodegradable compounds and relatively large reaction rate coefficients positively affect the efficiency of pollutant removal.

**Keywords:** COD fractionation, domestic wastewater, individual wastewater treatment plant, small wastewater treatment plant

## Introduction

Organic substrates in raw domestic wastewater are highly differentiated. Simple and complex compounds flow into the wastewater treatment plant in dissolved or suspended form. Accordingly to the susceptibility to biodegradation, these compounds can be divided into readily biodegradable compounds (carbohydrates, proteins and fats) and slowly biodegradable compounds (inert compounds). During the treatment they are transformed into simple compounds, are oxidized, assimilated, or are not decomposed. The division of the organic fraction regarding form and degradability is shown in Fig. 1 [1].

*e-mail: mmak@up.poznan.pl
**e-mail: marsp@up.poznan.pl

A significant difference was observed for filtered (by 0.45 μm pores nitrocellulose membrane) and unfiltered COD by Gajewska and Ambroch [2] in wastewater pretreated in a three-chamber settlement tank (average hydraulic retention time was two days): 283.6 g/$m^3$ and 660.3 g/$m^3$, respectively.

In the biochemical process the readily biodegradable organic compounds are 50% transformed into the biomass. The slowly biodegradable organic compounds are eliminated by microorganisms at long sludge retention times (SRT), whereas the inert compounds are adsorbed or precipitated [3].

Composition of the organic substrates in the wastewater is differentiated. It has an impact on biological degradability of wastewater. The wastewater flowing into the small wastewater treatment plant often originates from individual

Table 1. Content of COD fraction in raw wastewater reported in the literature.

| Fraction | Sources | | | | | | |
|---|---|---|---|---|---|---|---|
| | Kappeler and Gujer [12] | Henze et al. [13] | Mąkinia et al. [14] | Ekama et al. [15] | Rieger et al. [16] | Orhon et al. [17] | Other studies [5, 18-20] |
| $S_S$ | 7÷11 | 15÷32 | 5.4 | 20÷28 | 4 | 7÷32 | 11÷40 |
| $S_I$ | 10÷20 | 2÷11 | 27.4 | 5÷10 | 10 | 2÷20 | 1÷6 |
| $X_S$ | 53÷60 | 40÷49 | 48 | 60÷65 | 66 | 40÷77 | 41÷77 |
| $X_I$ | 7÷15 | 10÷20 | 19.2 | 4÷13 | 20 | 30÷60 | 11÷19 |

households and has a composition different from municipal wastewater. The rotten wastewater from holding tanks contains high loads of pollutants. The wastewater originating from an on-site wastewater treatment plant, preliminarily treated in septic tanks, contains a small amount of carbon compounds in relation to nitrogen compounds [4].

## Organic Compounds' Fractions in Wastewater

The content of readily biodegradable organic compounds depends on the substrate concentration, amount and activity of microorganisms, temperature, and presence of inhibitors [5]. BOD determination is proceeded at 20ºC temperature within the specified period of time. During the first five days 50-95% of organic compounds is oxidized. Therefore, $BOD_5$ determines the readily biodegradable organic substrate. The 5-50% residual of organic compounds is decomposed within the next 15 days. $BOD_{20}$ determines the sum of slowly and readily biodegradable organic substrates.

The first phase of the kinetics of decomposition can be expressed by the first-order reaction equation [6, 7]:

$$BOD_t = BOD_{tot} \cdot \left(1 - e^{-k \cdot t}\right) \qquad (1)$$

...where:

$BOD_t$ – biochemical oxygen demand after time $t$, ($gO_2/m^3$)

$BOD_{tot}$ – total biochemical oxygen demand for phase 1, ($gO_2/m^3$)

$k$ – reaction time constant, ($d^{-1}$)

$t$ – time, (d)

Nitrogen compounds oxidation, which may occur in two stages, is intentionally inhibited by thiosinamine.

The characteristic parameter is the reaction rate constant $k$, which can be determined experimentally or calculated accordingly to van't Hoff-Arhenius equation [8]:

$$k_T = k_{20} \cdot 1{,}047^{(T-20)} \qquad (2)$$

...where:

$T$ – temperature of sewage, (ºC)

$k_T$ – reaction rate constant in temperature $T$, ($d^{-1}$)

$k_{20}$ – reaction rate constant in temperature 20ºC, ($d^{-1}$)

According to the literature data [9], the value of the constant k for raw wastewater can vary from 0.07 to 0.80 $d^{-1}$, and at 20ºC – from 0.12 to 0.46 $d^{-1}$. Therefore, the application of $BOD_5$ for the readily biodegradable substrate assessment, without accurately determining $k$ value, can result in significant error, because the $BOD_5$ value depends on the $k$ parameter. Accurate determination of the organic substrate composition in wastewater is possible only when $k$ value is determined.

Next the content of slowly and readily biodegradable organic compounds as a sum can be determined as COD. 90-100% of organic compounds is oxidized in catalyzed reactions [6]. This way the organic fraction of wastewater can be precisely determined as COD (1 g of dissolved organic substance ≈ 1.5 g of COD) [10].

Application of mathematical modeling to design, simulation and controlling of the biological wastewater treat-

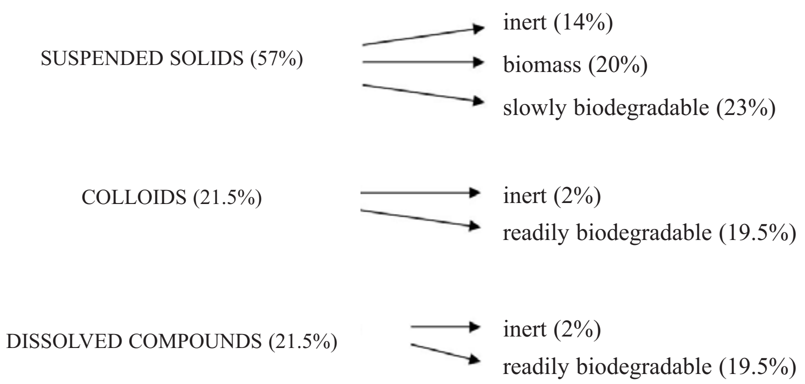


Fig. 1. COD fractionation in raw domestic wastewater [1].

Table 2. Technological characteristics of investigated treatment plants.

| Object | Technological steps | PE | Mean daily flow, $m^3/d$ | $BOD_5$ $gO_2/m^3$ | Volume, $m^3$ | | |
|---|---|---|---|---|---|---|---|
| | | | | | Primary settler | Reactor | Secondary settler |
| Individual WWTP Trzebisławki (2) | Primary settler + activated sludge reactor | 5 | 0.66 | 400 | 1.50 | 3.00 | |
| Individual WWTP Trzebisławki (7) | | 6 | 0.80 | 400 | 1.50 | 3.00 | |
| Individual WWTP Zielniczki (1) | Septic tank + trickling filter | 5 | 0.75 | 400 | 2.00 | 2.00 | |
| Individual WWTP Zielniczki (2) | | 6 | 0.90 | 400 | 2.00 | 2.00 | |
| Small WWTP Zielniki | Septic tank + activated sludge reactor | 183 | 22.0 | 500 | 7.85 | 15.00 | 3.10 |
| Small WWTP Chudzice | | 100 | 12.0 | 500 | 12.60 | 25.20 | 3.50 |
| Municipal WWTP Chwałkowo | Grit + activated sludge reactor | 24,450 | 3,925 | 400-650 | - | 5,000 | 2,814 |

ment systems, requires a division of the substrate to soluble and insoluble, biodegradable and unbiodegradable compounds [11]. The organic substrate expressed as COD, can be written as:

$$COD = S_S + X_S + S_I + X_I \tag{3}$$

...where:

*SS* – dissolved organic compounds, readily biodegradable, ($gO_2/m^3$)

$S_I$ – inert dissolved organic compounds, ($gO_2/m^3$)

$X_S$ – organic suspension slowly biodegradable, ($gO_2/m^3$)

$X_I$ – inert organic suspension, ($gO_2/m^3$)

The content of organic fraction, according to the literature, is shown in Table 1.

Content of particulate fractions can be calculated based on BOD, COD, and *k* coefficient (accordingly to ATV-131) [21]. The oxygen consumption test or respirometric test can also be used (accordingly to OECD 301F) [22]. Roeleved and Loosdrecht [23], Mąkinia et al. [14], and Czerwionka and Mąkinia [24] proposed to divide the dissolved and suspended phases mixture of organic contaminants by filtration or decantation. A problem is the classification of colloids. Some authors consider them suspended, other authors – dissolved compounds. Suspended fraction may thus be 65-79% or 57% of organic substrate.

## Investigated Treatment Plants

Seven different treatment plants located in Środa Wielkopolska district (Greater Poland) were selected for testing: two small treatment plants, four individual wastewater treatment plants, and one municipal wastewater treatment plant (for comparison). The design and technological parameters are shown in Table 2.

Individual wastewater treatment plants in Zielniczki (Zielniczki (1), Zielniczki (2)) received wastewater from households and utilized trickling filter technology. The mechanical treatment stage was septic tank equipped with a filter at the outlet. The biological treatment stage was a submerged trickling filter filled with basaltic pumice, aerated by the bottom disc diffusers and combined with the secondary settling tank. The treated wastewater was discharged into the soil by drainage. Wastewater samples were collected at the inlet and outlet of the biological reactor.

Individual wastewater treatment plants in Trzebisławki utilized a technology of low-loaded activated sludge. The systems contained the primary settling tank and the aerated chamber combined with the secondary settler. The treated wastewater was discharged into a drainage trenches. Wastewater samples were collected at the reactor inlet and outlet.

Small wastewater treatment plants in Zielniki and Chudzice received wastewater from local households. They consisted of a two-chamber primary settler, aerated chamber with aerobic stabilization, and secondary settler with chemical precipitation of phosphorus. The treated wastewaters were discharged into the drainage trenches. Wastewater samples were collected at the inlet, at the septic tank outlet, and at the reactor outlet.

The municipal treatment plant in Chwałkowo received wastewater form Środa Wielkopolska. The mechanical part was equipped with a pumping station and longitudinal grit chamber. The biological treatment stage was the phosphorus removal chamber with sludge recirculation and closed-loop reactor, with nitrification and denitrification. Treated wastewater was discharged into a canal and further into the Moskawa River. Wastewater samples were collected after the subsequent treatment stages.

## Experimental Procedure

Fractions of pollutants in wastewater were determined using ATV standard methods [21]. In this purpose, COD and $BOD_5$ were measured and the reaction rate constant (eq. 1) was determined. Organic fractions (eq. 3) were calculated as follows:

- $S_I$ – as 90% of COD of filtered treated wastewater
- $S_S$ – as the difference between COD for raw filtered wastewater ($S_{COD}$) and $S_I$:

$$S_S = S_{COD} - S_I \qquad (4)$$

- $X_S$ – taking into account $k$ – coefficient and correction factor $f_{BOD}$ = 0.15 (due to the transformation of the biodegradable compounds into the inert fraction):

$$X_S = 1/(1 - f_{BZT}) \cdot BOD_5 \cdot k_1 - S_S \qquad (5)$$

...where: $$k_1 = \frac{1}{1 - e^{-kt}} \qquad (6)$$

- $X_I$ – from the equation (for domestic sewage by ATV: $A$ = 0.25):

$$X_I = X_S / (1 - A) - X_S \qquad (7)$$

A similar calculation methodology was presented by Zawilski and Brzezińska [25] and Myszograj and Sadecka [18]. Reaction rate constant $k$ (eq. 1) was determined at 20ºC. In this aim, a measurement of $BOD_5$ for unfiltered wastewater with the addition of the nitrification inhibitor was carried out for 15 days in three replications. Constant $k$ was calculated according to equation 1, using the Polymath program, as an average of the three obtained values. Sample graph is shown in Fig. 2. Also, the efficiency of organic compounds removal in the investigated treatment plants was calculated. Relationships between treatment efficiency and biodegradable compounds content and temperature were found.

## Results and Discussion

Wastewater samples were collected in three series: in autumn (at 8-20C) I, in winter (at 3-4ºC) II, and in summer (at 19-27ºC) III. In each series three samples were collected. Fractions of organic pollutants for all samples were determined according to the above-described methodology.

The biodegradable organic compounds ($S_S$+$X_S$) in raw wastewater from treatment plants in Zielniczki contain 67-90% of COD (Fig. 3).

The high fraction of dissolved compounds (up to 67%) could be caused by the septic tank filter (at the outlet). A high concentration of $X_S$ was observed in outflow, especially in autumn and in winter. This could be caused by the low rate of hydrolysis at low temperatures.

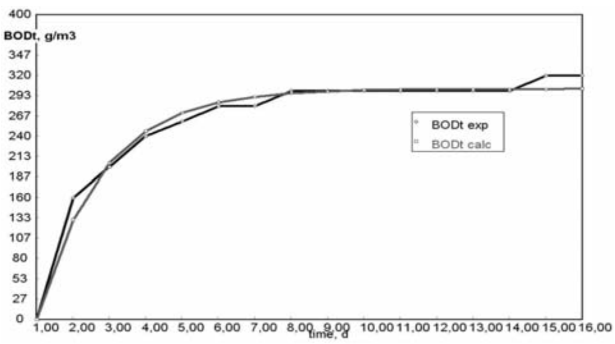


Fig. 2. Determination of $k$ and $BOD_{tot}$ using Polymath program.

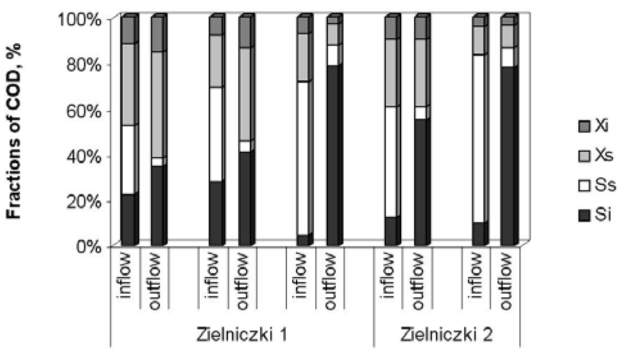


Fig. 3. COD fractions for individual treatment plants in Zielniczki during series I, II, III.

In the raw wastewater treated in individual treatment plant in Trzebisławki the content of biodegradable compounds in suspended solids was even greater: 80-89%, and was similar to content of dissolved biodegradable compounds: 63-71% (Fig. 4).

This could be caused by the nature of the source of wastewater and by high efficiency of primary settling tank. This indicated a high biodegradability of the wastewater. The content of $S_S$ fractions amounted to a few percent and $X_S$ fraction was below 20%, which indicated a high removal efficiency of biodegradable organic compounds. For all four investigated individual treatment plants efficiency of COD removal was equal to 55-94%.

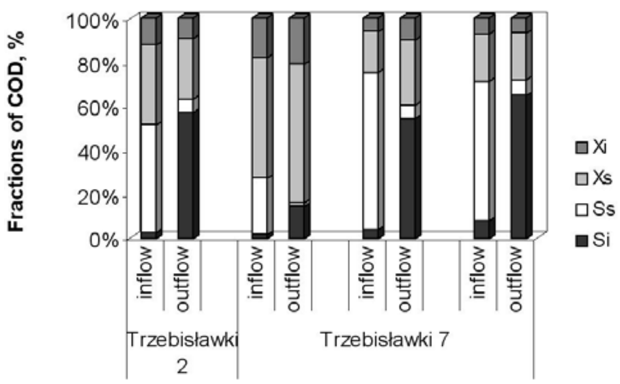


Fig. 4. COD fractions for individual treatment plants in Trzebisławki during series I, II, III.

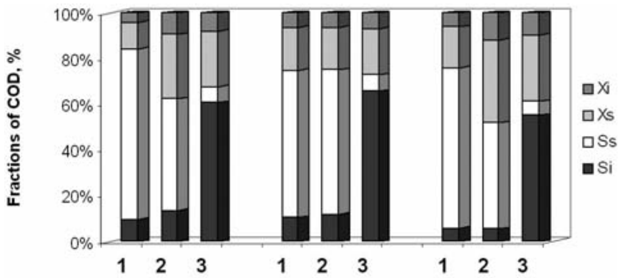


Fig. 5. COD fractions for small treatment plant in Zielniki during series I, II, III; 1 – inflow, 2 – septic tank effluent, 3 – outflow.

In the raw wastewater flowing into the small treatment plant in Zielniki an extremely high content of dissolved organic, readily biodegradable compounds ($S_S$ fraction) was found – from 64 to 74% (Fig. 5). This indicated the high biodegradability of this wastewater. Fraction of $X_S$ was equal to several percent of organic compounds only. Removal efficiency of total COD achieved 90%. Such composition of wastewater was probably caused by the nature of wastewater source and hydrolysis of suspended fraction in the sewage network. Concentrations of $X_S$ decreased after other treatment steps, which indicated the good efficiency of primary settling tank and biological treatment reactor. Removal efficiency of total COD achieved 84-87%.

Composition of the organic substrate in the raw wastewater flowing into the small wastewater treatment plant in Chudzice was different from the raw wastewater flowing into the treatment plant in Zielniki (Fig. 6). The fraction of $S_S$ in wastewater in Chudzice WWTP was much smaller (24-60%) than in wastewater in Zielniki WWTP. The $X_S$ fraction was similar in both WWTPs. $X_S$ in septic tank effluent was almost twice lower than in the influent to the septic tank (Fig. 6). The investigated wastewater contained about 80% of biodegradable fractions. This indicated a high biodegradability of these pollutants. Removal efficiency of total COD reached 85%.

The composition of organic pollutants in wastewater outflowing from the treatment plant in Chwałkowo was similar in all series of research. Fig. 7 shows the percentage of COD fraction after subsequent treatment steps in III

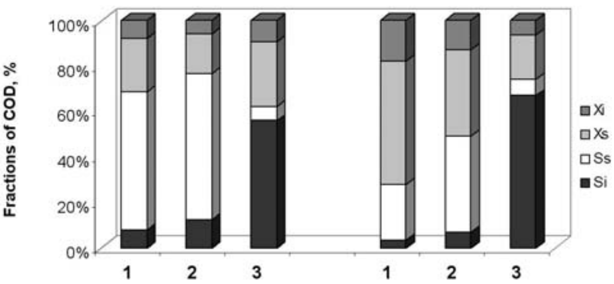


Fig. 6. COD fractions for small treatment plant in Chudzice during series I, II; 1 – inflow, 2 – septic tank effluent, 3 – outflow.

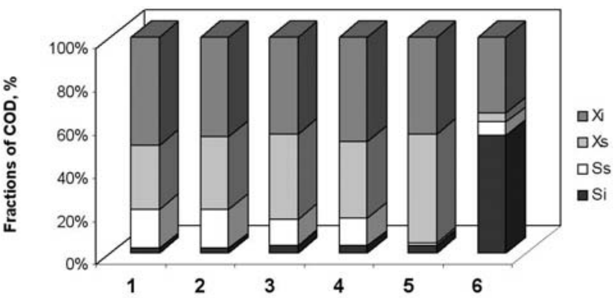


Fig. 7. COD fractions for municipal WWTP in Chwałkowo during series III; 1 – outlet from screen, 2 – outlet from grit chamber, 3 – inlet to defosfatation tank, 4 – outlet from defosfatation tank, 5 – outlet from aeration tank, 6 – outflow.

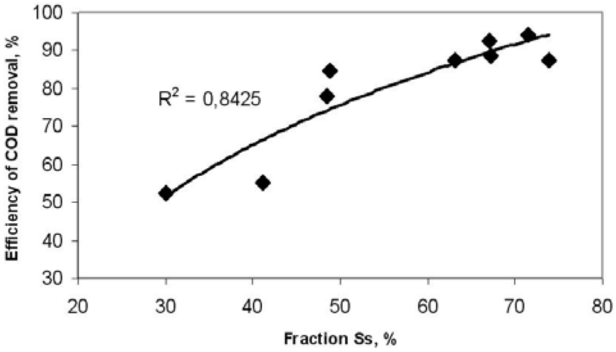


Fig. 8. Relationship between $S_S$ fraction and efficiency of COD removal for individual treatment plants in Zielniczki and Trzebisławki.

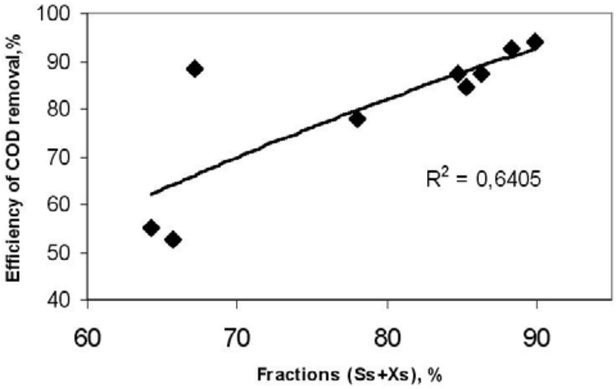


Fig. 9. Relationship between fraction of sum of $S_S$ and $X_S$ and efficiency of COD removal for individual treatment plant in Zielniczki and Trzebisławki.

series of research. The characteristic of raw wastewater was a small content of $S_S$ fraction and common content of $X_S$ fraction. Biodegradable fractions reached up to 50%, which indicated the relatively high biodegradability of wastewater. The removal efficiency of organic compounds was equal to 99% for $BOD_5$ and to 89% for COD. Hydrolysis of the suspended solids was relatively slow, because the removal of organic suspended solids took place only in the aeration chamber. The highest reduction of inert suspended organic compounds occurred in the secondary clarifier. This indicated a sorption of the suspended substrate on activated sludge flocs. Total COD was removed in 80%. Observed values were similar to the values specified by other authors, but $X_S$ fraction was much smaller than in other Polish WWTPs (Table 1). Similar values were obtained by Myszograj and Sadecka [18] and Płócienik-Koropczuk [19] for WWTPs in Sulechów and Zielona Góra.

Also, the relationship between COD removal efficiency and biodegradable fraction ($S_S$ and $X_S$) in raw wastewater was determined (Figs. 8 and 9). Significant correlation for individual treatment plants was observed between the organic dissolved biodegradable fraction ($S_S$) and the sum of biodegradable fraction ($S_S$+$X_S$) and COD efficiency.

For small WWTPs located in Zielniki and Chudzice, significant correlation was obtained only between the con-

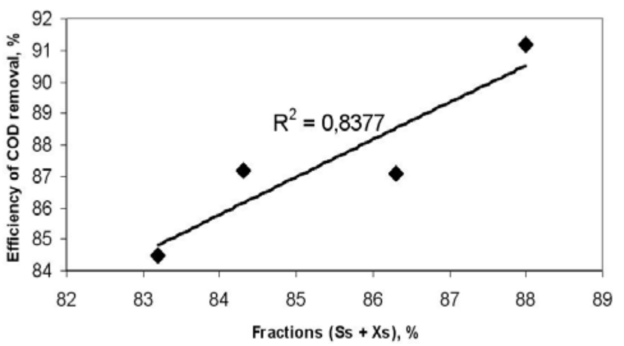


Fig. 10. Relationship between fraction of sum of $S_S$ and $X_S$ and efficiency of COD removal for small treatment plants in Zielniki and Chudzice.

tent of biodegradable fractions ($S_S$+$X_S$) and removal efficiency of COD (Fig. 10). Organic pollutants removal efficiency also increased with the content of biodegradable fractions in wastewater.

Based on the determination of the organic fractions in wastewater, reaction rate coefficient (*k*) was calculated. For raw wastewater flowing into the individual treatment plant, mean values ranging from 0.12 to 0.27 $d^{-1}$ (maximum 0.35 $d^{-1}$) were obtained. These values (Fig. 11) corresponded with range reported in the literature [26].

The discrepancy between the values of the *k*-coefficient is the result of differentiated composition of the wastewater. Some of the received values exceeded the typical values reported in the literature. This confirmed the good susceptibility of wastewater for biodegradation.

## Conclusions

The wastewater originated from small communities and households differing significantly in composition from municipal wastewater. It contains much more organic dissolved biodegradable fraction $S_S$ (60-75%) than municipal wastewater (up to 20%). Organic slowly biodegradable suspended fractions $X_S$ were comparable or slightly lower in both types of WWTP (20-55% in small community and household WWTPs and up to 30% in the Chwałkowo WWTP). Total biodegradable organic compounds in the analyzed samples usually exceeded 70%. In comparison to the results obtained for WWTP in Chwałkowo and literature data, the values obtained in this study for small and individual WWTPs were two times higher (this can be explained by the fact that in small sewer systems there is no fermentation of wastewater). A large percentage of organic biodegradable compounds indicates a good susceptibility of wastewater for biological treatment. Relatively high values of reaction rate coefficient *k* also indicate good susceptibility of wastewater for biodegradation.

The efficiency of organic compounds removal in small and individual wastewater treatment plants is significantly dependent on the content of biodegradable fractions. The results of this study show that at high rates of biodegradable fraction in wastewater the small and individual WWTPs reach high efficiency (comparable to the municipal WWTPs).

Organic compound fractionation in wastewater and in septic tank effluent may be useful or even necessary for modeling biological treatment in various systems or in various environments, e.g. activated sludge reactors [27], anaerobic organic matter transformations in the sewer networks [28], and tertiary nitrification during biofiltration of municipal wastewater [29].

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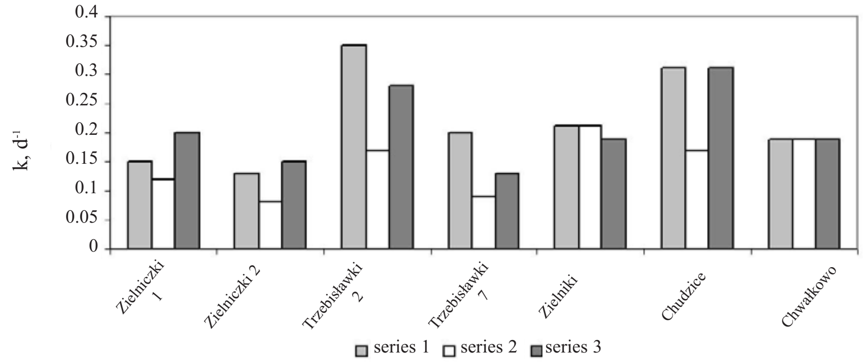


Fig. 11. Reaction rate k-coefficient for wastewater from investigated treatment in three series of research.

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