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# Estimation of Chemical Oxygen Demand Fractions of Municipal Wastewater by Respirometric Method – Case Study

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## 1. Introduction

Nowadays, a detailed characterization of influent wastewater is one of the most relevant factor to efficient operation of wastewater treatment plants (WWTPs). Moreover, in recent years, the increasing utilization of plant simulation models such a ASMs (activated sludge models) developed by IWA (IAWQ Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment Processes) required accurate and precise description of raw wastewater, especially organic matter presented in the inflow [1, 2]. Traditionally, those compounds were characterized by COD (chemical oxygen demand), BOD (biological oxygen demand) and TOC (total organic carbon) parameters, but only division of COD into fractions with different microbiological properties gives more precise information on the biodegradation of the carbonaceous substrate [3, 4]. The total COD ($C_T$) is divided into two main fractions: biodegradable ($C_S$) and nonbiodegradable (inert) ($C_I$). The biodegradable COD is further divided into readily biodegradable substrate ($S_S$) and slowly biodegradable, particulate substrate ($X_S$) [5–7]. The readily biodegradable substrate consists of simple soluble compounds such as volatile fatty acid, alcohol etc. which can be easily absorbed by organisms and metabolized for energy and synthesis [8, 9]. The slowly biodegradable fraction is mainly composed of particulate, colloidal and complex organic molecules. In case of this fraction, many of these components could be absorbed and utilized only after the hydrolysis by extra cellular enzymes of bacteria [7, 10]. The nonbiodegradable soluble substrate is transferred in the effluent without any significant modification. The particulate inert fraction ($X_I$) is mostly accumulated in the activated sludge and removed from the system with primary and secondary sludge [11].

Several methods have been proposed for estimation COD fractions, but only respirometric and physical-chemical techniques have most commonly been applied. The physic-chemical methods used processes such as filtration and flocculation to separate particulate fractions. The main disadvantage of this technique is that those processes couldn't effectively divide the biodegradable substrates ($S_S$ and $X_S$). On the other hand, the physic-chemical methods are relatively fast and facile [11, 12]. The respirometric measurement is based on analysis of the biological oxygen consumption rate (OUR) under well-defined experimental conditions [5, 13]. This method demands special equipment and its more time consuming. Whereas this technique allows for obtaining more accurate data for research studies as well as for preparing wastewater treatment plant simulations [11, 14–16].

Furthermore, the chemical oxygen demand fractionation was not only used in the case of activated sludge models to increase the understanding of the effect of process changes or fluctuations on the treatment process efficiency, but also for modeling of wastewater transformation and biodegradation during the transport in sewer systems. Currently, these processes are quite well recognized and mentioned as important factor influenced the operational parameters of WWTP. This is mainly due to the fact that in sewer conduits significant part of biodegradable substances could be removed from wastewater and buildup into sewer biofilm or suspended microorganism biomass [17, 18]. In that situation at the WWTP can appear problems with proper substrate equilibrium C/N/P demanded for biological treatment of wastewater from carbon and biogenic substances. On the other hand, models of sewage biodegradation can be used to predict discharge of pollutants load into the receiver – mainly river form storm water system or combined sewer system. In that situation mentioned models can be also applied for increase and optimize processes of sewage biodegradation by provide proper dissolved oxygen concentration e.g. by wastewater reaeration in conduits, appropriate time of flowing and proper condition for sediments transport etc [17–19].

The main aim of this study is to determine COD fractions both in raw wastewater and in reject water obtained from municipal wastewater treatment plant in Malaga, Spain.

## 2. Materials and methods

Samples of wastewater and activated sludge were taken from municipal wastewater treatment plant Guadalhorce (145 000 $m^3$/d) in Malaga, Spain. The wastewater was taken from four collectors, three of them (A, B, C) collected raw municipal wastewater from different district of the city. The last one (D), recycled wastewater produced during sewage sludge treatment (Fig.1). A detailed description of collectors is shown in Table 1. Moreover, it could be noted that the research was conducted during the summer with high temperatures and absence of rain.

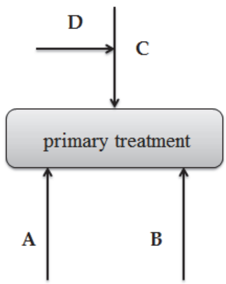


**Fig. 1.** Illustration of influent collectors to WWTP
**Rys. 1.** Kolektory wprowadzające ścieki do oczyszczalni

The experiment was carried out using a respirometer BM – T (Surcis). The equipment consisted of three main parts: batch reactor with the volume 1.0 $dm^3$ (BM-T analyzer), thermostatic unit and computer. The respirometer was inoculated with activated sludge from one of the biological reactors. This sample was aerated over 24 hours before the measure to reach the endogenous respiration. For all measurements the temperature was maintained at 20.0 ± 0.1°C and pH was kept in the range 7.0 and 8.0. For all batch tests, freshly collected samples (max 2 hours after collection) were used. Before the analysis (about 10 min) 10 ml solution of allylthiourea (ATU) was added to respirometer's chamber in order to eliminate oxygen consumption due to nitrification. The measurement was conducted in accordance with the procedure given by Surcis.

**Table 1.** The main characteristic of collectors
**Tabela 1.** Podstawowe cechy kolektorów

| Collector | Diameter [m] | Flow [$m^3/d$] | Length [m] | Collector type |
|---|---|---|---|---|
| A | 0.7 | 32000 | 3143 | pressure |
| B | 1.1 | 82000 | 5641 | pressure |
| C | 0.6 | 18000 | 10000 | gravity |
| D | 0.5 | 7000 | 100 | gravity |

The respirometer recorded directly two fractions: total biodegradable ($C_S$) and readily biodegradable ($S_S$) ($mg \cdot dm^{-3}$). The other fractions were defined by following calculations:

$$X_S = C_S - S_S \; [mg \cdot dm^{-3}] \quad (1)$$

$$S_I = S_T - S_S \; [mg \cdot dm^{-3}] \quad (2)$$

$$X_I = C_I - S_I \; [mg \cdot dm^{-3}] \quad (3)$$

where:
$S_I$ soluble inert COD substrate ($mg \cdot dm^{-3}$), $S_T$ total soluble COD ($mg \cdot dm^{-3}$), $X_I$ particulate inert substrate ($mg \cdot dm^{-3}$), $X_S$ slowly biodegradable organic matter ($mg \cdot dm^{-3}$), $C_I$ total nonbiodegradable COD ($mg \cdot dm^{-3}$).

In this study the percentage values of individual fractions were presented, therefore the obtained value of particulate fraction ($mg \cdot dm^{-3}$) was compared to the total concentration of COD ($C_T$) ($mg \cdot dm^{-3}$). Presented results are the average of five replicates.

In order to estimate ($S_T$) the total soluble COD, the samples of wastewaters were filtered through 0.45 μm filter, then the chemical oxygen demand was measured. All chemical oxygen demand ($S_T$ and $C_T$) analyses were performed with Hach Lange UV-VIS DR 5000 using Hach analytical methods.

## 3. Results and discussion

The results of presented study are shown in Figure 2. The readily biodegradable substrate ($S_S$) differed from 19.9 to 56.5 % of the total COD ($C_T$), the lowest share of this fraction was observed in collector D, which contributed wastewater from sewage sludge system. Estimations obtained for slowly biodegradable fraction of COD ($X_S$) varied from 4.2 to 16.6 %.

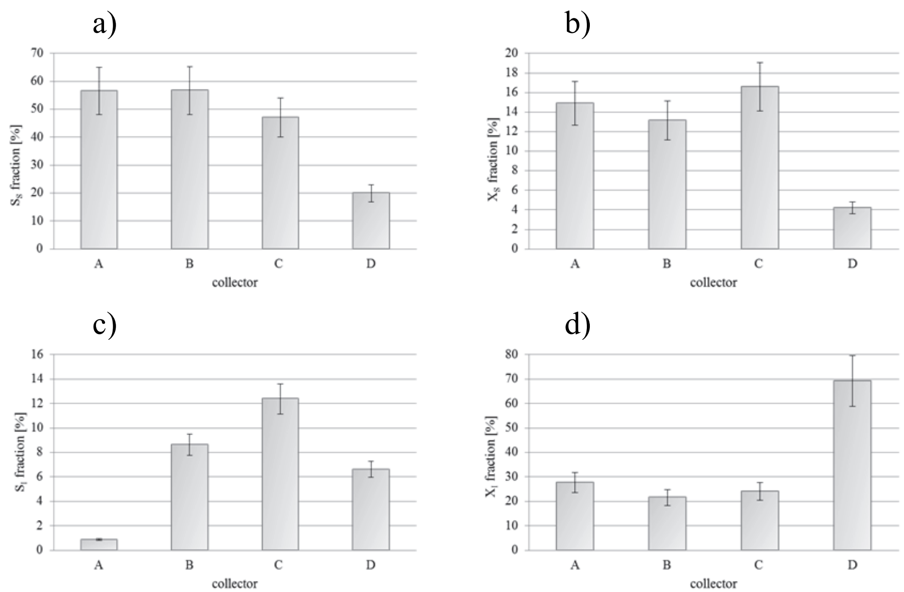


**Fig. 2.** Average values of a) $S_S$ b) $X_S$ c) $S_I$ d) $X_I$ fractions with standard deviation from different collectors
**Rys. 2.** Średnie wartości frakcji a) $S_S$ b) $X_S$ c) $S_I$ d) $X_I$ wraz z odchyleniem standardowym w poszczególnych kolektorach

As in case of readily biodegradable organic fraction, the smallest value of total COD was obtained from collector D. The wastewater from collectors A, B and C was characterized by low concentration of inert fractions, form 0.9 to 12.4% for inert soluble substrate and from 21.6 to 27.8% for inert suspended substrate. As shown in figure 2. c and d, the reject water had a significant share of non-biodegradable fractions, especially the particulate inert fraction, $X_I$ = 69% of total COD.

**Table 2.** The summary of COD fractions from various countries (raw wastewater)
**Tabela 2.** Zestawienie frakcji ChZT z różnych krajów (ścieki surowe)

| Country | $S_S$ | $X_S$ | $S_I$ | $X_I$ | References |
|---|---|---|---|---|---|
| | % | | | | |
| S. Africa | 20.00 | 62.00 | 5.00 | 13.00 | [5] |
| | 25.00 | 53.00 | 7.00 | 15.00 | [31] |
| Switzerland | 10–20 | 53–60 | 7–11 | 7–15 | [6] |
| Spain | 18.3 | 33.3 | 8.5 | 24.9 | [32] |
| Netherlands | 41.50 | 32.70 | 4.70 | 16.60 | [20] |
| Germany | 26.00 | 57.00 | 3.00 | 14.00 | [33] |
| Turkey | 26.00 | 62.00 | 2.00 | 10.00 | [14] |
| Poland | 23–29 | 51–56 | 2–3 | 17–19 | [34] |
| | 21–40 | 34–51 | 4–7 | 21–28 | [35] |
| Denmark | 35.0 | 35.0 | 5.0 | 10.0 | [36] |
| Italy | 12.2–0.3 | 27.6–66.9 | 1.2–14.0 | 8.8–33.1 | [21] |
| Hungary | 21.9 | 49.8 | 4.6 | 23.7 | [11] |

The obtained results of COD fractioning from WWTP in Malaga were substantially different from those presented in literature (Table 2), particularly in case of readily biodegradable fraction in collectors A, B and C. Frequently, the percentage of this fraction is varied from 10 to 20% of $C_T$. However, in the study conducted by van Veldhuizen et al. [20] and Quevauviller et al. [21] similar data was observed.

The high concentration of this fraction in municipal wastewater might have a beneficial influence on denitrification as well as the biological phosphorus removal process [22, 23]. Hydrolyzed lipids, however, could cause the growth of filamentous bacteria [23, 24]. Moreover, in the study performed for pipelines A, B and C inert fractions of total COD ($S_I$ and $X_I$) were comparable to the typical value provided by researches from different countries.

The collector D was characterized by a significant share of nonbiodegradable fractions (more than 70% of $C_T$). This pipeline contributes the reject water, which could be defined as a high-strength wastewater, produced during sewage sludge treatment. Because of high nitrogen and phosphorus load as well as a significant amount of nonbiodegradable organic load [25], those sidestreams have a major impact on WWTP performance [26, 27]. Generally, reject water is recycled to the head of the wastewater treatment plant without any pretreatment, which could cause several problems in WWTP such a process upset, release of odors, violation of discharge limits and increased operational and maintenance costs [28, 29].

The percentage share of particular fractions depends on various factors. According to Quevauviller et al., [21] the value of readily biodegradable COD ($S_S$) as well as particulate inert COD ($X_I$) is related to the capacity of wastewater treatment plant and share of industrial wastewater in the influent. In case of large WWTPs, the lower percentage of $S_S$ and a higher percentage of $X_I$ might be observed. This fact is associated with the retention time of wastewater in sewage systems. Usually the larger WWTPs have more complex sewer collection system with a longer retention time of wastewater, therefore the transformation and biodegradation process occur at bigger scale in pipelines. Besides, the higher share of inert substrate in total COD is generally linked with presence of industrial wastewater. Moreover, the type of sewer systems has significant influence on the value of particulate fractions [4]. The wastewater from combined sewer has a more varied composition than in case of separate systems. Zhou et al. (2008) shown that the lower percentage of readily biodegradable fractions were caused by the dilution effect of stormwater runoff [29]. Moreover, in the study conducted by Zhou et al. proved the influence of industrial wastewater overflows on COD fractions. Additionally, the presence of accidental and infiltration water could provide a noticeable change of wastewater character.

## 4. Summary and conclusions

The division of COD into fractions with different microbiological properties is comprehensive tool for wastewater characterization. It could be applied to control and modeling of wastewater treatment plants and sewer systems functioning. Furthermore, it gives faster result about the presence of biodegradable substrate in raw wastewater in comparison to biological oxygen demand (BOD). The COD fractionation could give much useful information about the condition of sewer systems, particularly about contribution of infiltration water and industrial wastewater discharges.

In this study the COD fractions in municipal wastewater from various collectors and in reject water were presented. In case of raw municipal wastewater (collectors A, B and C) biodegradable fractions were dominated, from 47 to 57% for readily biodegradable fraction and from 13 to 16% for slowly biodegradable fraction. The reject water from

MWWTP (collector D) was characterized by a significant share of non-biodegradable fractions, the percentage of particulate inert fraction was 69% and the percentage of inert soluble fraction ranged 6.7%.

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# Wyznaczenie frakcji ChZT w ściekach komunalnych z wykorzystaniem metody respirometrycznej


## Streszczenie

Jednym z ważniejszych problemów z punktu widzenia sterowania pracą oczyszczalni ścieków jest posiadanie kompletnych i dokładnych informacji na temat jakości ścieków. Do oceny parametrów jakościowych ścieków stosowane jest określanie udziałów frakcyjnych chemicznego zapotrzebowania na tlen (ChZT) pod względem właściwości fizycznych oraz podatności na biodegradację. Informacja na temat udziałów frakcyjnych ChZT może być wykorzystywana w modelowaniu pracy systemów oczyszczania ścieków jak również modelowania procesów transportu i biodegradacji zanieczyszczeń w systemach kanalizacyjnych. Opracowanie prezentuje wyniki badań udziałów frakcyjnych ścieków dopływających do miejskiej oczyszczalni ścieków w Maladze (Hiszpania). Ścieki surowe dopływały do kolektora zbiorczego z różnych dzielnic miasta kolektorami oznaczonymi jako A, B oraz C, natomiast kolektorem D doprowadzane były wody z gospodarki osadowej, zawracane na początek procesu technologicznego oczyszczalni. Do wyznaczenia udziałów frakcyjnych ChZT w analizowanych próbkach ścieków wykorzystane zostały metody respirometryczne. W przypadku ścieków surowych największy udział w całkowitym ChZT miała frakcja biodegradowalna, 47–57% przypadało na frakcje szybko ulegające biodegradacji, natomiast 13 do 16% na frakcje wolno ulegające biodegradacji. Odcieki z urządzeń gospodarki osadowej charakteryzowały się znacznym udziałem frakcji nieulegających biodegradacji, przy czym 69% przypadało na frakcje w postaci zawiesiny, natomiast 6,7% w postaci rozpuszczonej.



**Słowa kluczowe:**
frakcje ChZT, materia organiczna, modele symulacyjne

**Keywords:**
COD fractions, organic matter, wastewater plant simulation models