

## Chemical oxygen demand fractions of municipal wastewater for modeling of wastewater treatment

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**ABSTRACT:** When a new wastewater treatment plant is being designed by computer simulation, detailed data about organic fractions of influent wastewater (measured as chemical oxygen demand) are usually not available, but knowledge of the typical ranges of these fractions is indispensable. The influent chemical oxygen demand fractions can substantially influence the results of simulation-based design such as reactor volumes, solids residence time, effluent quality, oxygen demand, sludge production, etc. This article attempts to give an overview of wastewater organic fractions as modeling parameters and presents new chemical oxygen demand fractionation results from Hungary. According to the data from literature, the ratio of chemical oxygen demand components in raw wastewater is very different and the average composition is as follows: Inert particulate = 17.1 %, slowly biodegradable = 57.9 %, inert soluble = 7.8 % and readily biodegradable = 17.5 %. The Hungarian wastewater samples were analyzed according to STOWA (Dutch foundation for applied water research) protocol and the obtained results were not much different from those of literature (inert particulate = 23.7 %, slowly biodegradable = 49.8 %, inert soluble = 4.6 % and readily biodegradable = 21.9 %), but some typical characteristics were observed.

**Key words:** *Simulation, activated sludge models, sewage, characterization*

### INTRODUCTION

Use of the activated sludge models (ASM) in wastewater treatment plant (WWTP) simulation is widespread. Nowadays, the design of activated sludge WWTPs is based on simulation studies instead of the empiric formulas.

#### *Base data availability for designers*

In the case of new WWTP design when wastewater samples are not available for characterization, the level of model calibration is quite low. In such cases only literature data, default values and assumptions can provide the base information needed to set influent characteristics and biokinetic parameters (Vanrolleghem *et al.*, 2003). The assumed influent Chemical oxygen demand (COD), N, P fractions can substantially influence the results of simulation-based design such as reactor volumes, solids residence time, effluent quality, oxygen demand, recirculation rates, sludge production, etc. Many publications are available on wastewater characterization, but not a single review article on COD fractions can be found. That is why summarizing the published data on wastewater

composition is important in design practice and thus in achieving accuracy in WWTP design.

#### *Division of organic matter*

Generally, influent N (ammonium, nitrate, total nitrogen) and P (orthophosphate, total phosphorous) fractions can be assessed easily because they are routinely measured in every WWTP. Moreover, characterization of nitrogen and phosphorous fractions is not necessary in as much detail as for COD because the major part of influent nitrogen is present in ammonia and most of the phosphorous occurs in orthophosphate form. In ASM1 and ASM3 models, the total influent COD ( $COD_{TOT}$ ) of the wastewater is divided into seven fractions and in ASM2 and ASM2d models into nine (Henze *et al.*, 1987; 1995; 1999; 2000). The most important influent COD fractions, which are used as component variables in activated sludge models, are shown in Fig. 1.

#### *Determination of COD fractions*

Several methods have been developed for wastewater characterization, but the two most

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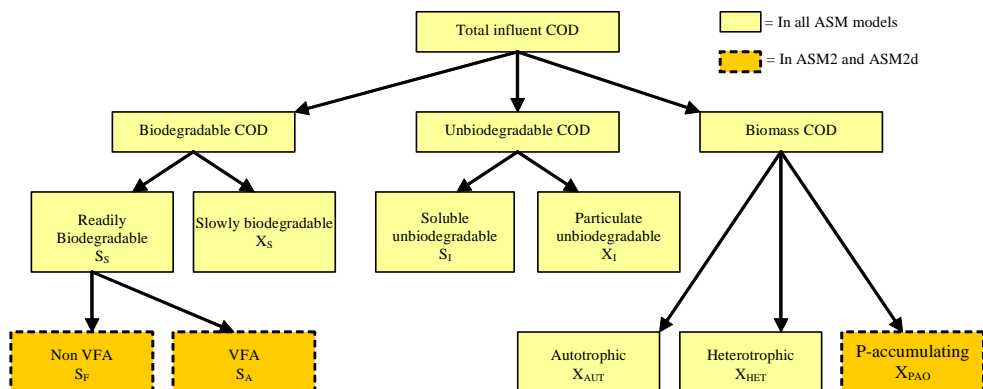


Fig. 1: Division of influent wastewaters into COD components in ASM model family

commonly used processes are the biological and physical-chemical characterizations. The biological or respirometric characterization method is based on the measurement of the biomass response during substrate degradation in either continuous flow or batch type experiment. The recorded utilization rate of the dissolved oxygen or nitrate (for denitrification potential) is closely related to the quality and quantity of available substrate in the system (Spanjers *et al.*, 1995). This method needs experienced and skilled laboratory staff, specific experimental appliances and usually model-based interpretation. It may provide higher accuracy and is therefore more suitable for research studies. The physicochemical method is based on the assumption that COD fractions model can be separated by filtration and flocculation processes and that COD of the gained fractions is easily measurable by standard chemical methods (Mamais *et al.*, 1993). The main problem of this process is that the filtration can not effectively separate readily and slowly biodegradable fractions because the colloidal (between soluble and particulate) matter may contribute to both fractions. The combined physical-chemical and biological method of STOWA (Dutch foundation for applied water research) includes both filtration and flocculation steps with COD and BOD measurements (Roeleveld and Loosdrecht, 2002). This method is quick and easy to use, but it completely neglects biomass fractions. Also, the information provided on  $X_I$  fraction could be false because the fraction is determined by the remainder in the last characterization step [inert particulate ( $X_I$ ) =  $COD_{TOT} -$  slowly biodegradable ( $X_S$ ) – readily biodegradable ( $S_S$ ) – inert soluble ( $S_I$ )]. The inaccuracies of the first determined fractions can be reflected in  $X_I$  (Melcer *et al.*, 2003). The simplicity and cheapness of this method make it suitable for new simulation users

and consultants (Sin *et al.*, 2005).

## MATERIALS AND METHODS

The aim of this study was to collect and summarize the data of wastewater COD fractions from several countries, including Hungary and to provide default modeling parameters to WWTP designers. First, the wastewater characteristics of different countries were collected from literature and then their COD fractions were summarized separately as primary (settled) and raw wastewater data (Tables 1 and 2). Concurrently, COD fractions of the influent sewage of 11 Hungarian WWTPs were determined using the STOWA protocol treating municipal wastewater with only minimal industrial contribution (Roeleveld and Loosdrecht, 2002). Twenty-four-hour composite samples of influent wastewater were collected after screening, but before primary sedimentation or any kind of biological treatment. Final effluent samples were collected at the outlet of the secondary sedimentation tanks before disinfection. The capacities of examined WWTPs were between 100 and 15,000 m<sup>3</sup>/d with 12-20 d solid retention time.

### The main steps and theoretical formulas of COD fractionation

$S_I = 90$  % of filtered (0.45  $\mu$ m) effluent COD;  $S_S =$  Flocculated ( $ZnSO_4$ ) and filtered (0.45  $\mu$ m) influent COD –  $S_I$ ;  $S_A =$  Measured by ionchromatography from influent sewage;  $S_F = S_S - S_A$ ;  $X_S = BOI_{ULTIMATE} - S_S$ ; ( $X_I$ ) =  $COD_{TOT} - S_I - S_S - X_I$

Measurement of COD and BOD was carried out following standard methods. The measured influent COD fractions of the two examined WWTPs were validated by computer simulation which yielded good correlation.

## RESULTS AND DISCUSSION

### *Ranges of ASM COD fractions from design viewpoint* *Readily biodegradable substrate*

( $S_s$ ) is the most easily available COD fraction for heterotrophic microorganisms. The quantity of  $S_s$  can be a determining factor for anaerobic and anoxic reactor volumes in model-based design because the processes of phosphate release and denitrification are very sensitive to the easily accessible substrate fractions.

According to scientific data, readily biodegradable substrate ranges between 3–35 % in raw wastewater and 14–57 % in settled wastewater (Lesouef *et al.*, 1992; Funamizu *et al.*, 1997; Chachaut *et al.*, 2005; Marquot *et al.*, 2006). In ASM2 and ASM2d models, this component is divided into volatile fatty acids (VFA = acetic acid, propionic acid, butyric acid, etc.) and non-VFA components (alcohols, lower amino acids, simple carbohydrates) (Henze, 1992). The VFA fraction ranges between 0–8.8 % in raw wastewater and 0–16 % in primary wastewater (Henze, 1992; Henze *et al.*, 1995; Satoh *et al.*, 2000; Hydromantis, 2007).

### *Slowly biodegradable substrate*

( $X_s$ ) component comprises complex organic compounds which need to be hydrolyzed by extra cellular enzymes of bacteria prior to utilization. This component is usually made up of colloidal and suspended COD fractions. That is why it can not be separated from influent samples solely by physical separation. From the design point of view, this fraction usually has the highest oxygen demand and therefore it greatly influences the air flow required to aeration tank.

This component ranges between 28–74 % in raw sewage and 24.5–65 % in primary wastewater (Solfrank, 1988; Lesouef *et al.*, 1992; Roeleveld and Loosdrecht, 2002; Marquot *et al.*, 2006).

### *Soluble unbiodegradable*

COD fraction ( $S_i$ ) can not be further biologically degraded in treatment plants and therefore the influent  $S_i$  COD leaves the plant without any significant change in its concentration. Because of the soluble inert fraction of sewage, WWTPs treating strong municipal wastewaters or septic tank effluents ( $COD_{TOT} > 1500$  mg/L) with even perfect carbon oxidation may find it hard to meet the strict COD effluent standards.  $S_i$  fraction, relative to the  $COD_{TOT}$ , is in the range of 2–15 % in raw wastewater and 3–14.3 % in primary sewage (Henze, 1992; Xu and Hultman, 1996; Satoh *et al.*, 2000).

### *Particulate unbiodegradable*

( $X_p$ ) component is not degraded biologically during the treatment process and hence it can be removed only by clarification. From designers' point of view, this fraction significantly influences the quantity of primary and secondary sludge and therefore it determines the required dewatering and sludge treating capacity. Raw wastewater and primary wastewater contain 8-39 % and 4–20 %  $X_p$ , respectively. (Ekama *et al.*, 1986; Henze *et al.*, 1987; Carucci *et al.*, 1999; Roeleveld and Loosdrecht, 2002).

### *Biomass COD*

In ASM2 and ASM2d models, bio mass is classified into three fractions: Heterotrophic biomass ( $X_H$ ); autotrophic biomass ( $X_{AUT}$ ) and phosphorous accumulating microorganisms ( $X_{PAO}$ ). COD fractions of  $X_{AUT}$  and  $X_{PAO}$  are generally not measured; their fractions in percent of  $COD_{TOT}$  are assumed to be about 1 % or less. Because of the low growth rate of autotrophic and phosphate accumulating organisms, their biomass fractions have to be considered in the modeled influent, otherwise, they can be washed out in high-loaded systems (Roeleveld and Loosdrecht, 2002).

Heterotrophic biomass may constitute a significant fraction in wastewater COD. The range of  $X_H$  is 7–20 % in raw wastewater and 3.5–25 % in primary settling tank effluent (Solfrank, 1988; Henze, 1992; Lesouef *et al.*, 1992; Gernaey and Jorgensen, 2004).

### *Summary of foreign and Hungarian COD fractions*

Data about the COD fractions of different studies were summarized separately as fractions of raw wastewater (Table 1) and settled wastewater (Table 2).

The results of Hungarian raw wastewater measurement are presented in Table 3. When the biomass fraction is not determined separately, as is often the case,  $X_H$  can be measured as  $X_s$ . Therefore, every Table has a ' $X_s (+X_H)$ ' column in which the biomass fraction is included in the 'slowly biodegradable organic fraction' to facilitate comparison of the data. The measured Hungarian average COD fractions in raw wastewater ( $X_i = 23.7$  %,  $X_s = 49.8$  %,  $S_i = 4.6$  %,  $S_s = 21.9$  %) are not much different from the corresponding values found in the literature of foreign countries ( $X_i = 17.1$  %,  $X_s = 57.9$  %,  $S_i = 7.8$  %,  $S_s = 17.5$  %) (Figs. 2 and 3). The values of COD fractions as seen in the foreign publications are very diverse and belong to the Hungary. Nevertheless, some typical characteristics can be observed in the values

Chemical oxygen demand fractions of municipal wastewater

Table 1: Summary of COD fractions of raw wastewater (literature data)

Country, region	S <sub>I</sub> %	S <sub>S</sub> %	X <sub>I</sub> %	X <sub>S</sub> %	X <sub>H</sub> %	X <sub>S</sub> (+X <sub>H</sub> )** %	VFA %	References
N. America	10.5	14.1	27.9			44.3	0.0	Hydromantis, 2007
S. Africa	5.0	20.0	13.0			62.0		Ekama <i>et al.</i> , 1986
Switzerland	14.0	9.0	9.0	56.0	12.0	68.0		Kappeler and Gujer, 1992
Denmark	2.0	20.0	18.0	40.0	20.0	60.0		Henze, 1992
Sweden	15.0	27.0	17.0	33.0	8.0	41.0		Xu and Hultman, 1996
Denmark	7.6	20.3	13.0	51.5	7.2	58.7	8.1	Gernaey and Jorgensen, 2004
Denmark	5.0	35.0	10.0	35.0	15.0	50.0		Chachaut <i>et al.</i> , 2005
N. America	12.0*	15.0	14.5*			59.0	1.4	Melcer <i>et al.</i> , 2003
Netherlands	6.0	26.0	39.0			28.0		Roeleveld and Loosdrecht, 2002
N. America	5.0	16.0	13.0			66.0	2.4	EnviroSim, 2005
France	4.1	3.0	19.0			73.9		Marquot <i>et al.</i> , 2006
Germany	6.4	18.3	11.3	49.3	14.7	64.0		Wichern <i>et al.</i> , 2003
Germany	6.1	14.8	13.0	55.4	10.8	66.2		Wichern <i>et al.</i> , 2001
Italy	6.0	15.0	8.0	56.0	15.0	71.0		Carucci <i>et al.</i> , 1999
Spain	8.5	18.3	24.9	33.3	15.0	48.3		Del la Sota <i>et al.</i> , 1994
Denmark	10.0*	15.0*	20.0	40.0*	15.0	55.0*	8.8	Henze, 1992
Switzerland	4.0	10.0	20.0	54.1	11.9	66.0		Rieger <i>et al.</i> , 2001
Average	7.5	17.5	17.1	45.8	13.1	57.9	4.1	

\* Estimate based on the article; \*\* Biomass COD is included in the slowly biodegradable substrate fraction

Table 2: Summary of COD fractions of primary wastewater (literature data)

Country, region	S <sub>I</sub> %	S <sub>S</sub> %	X <sub>I</sub> %	X <sub>S</sub> %	X <sub>H</sub> %	X <sub>S</sub> (+X <sub>H</sub> )** %	VFA %	References
Japan	14.3*	26.7	8.20	41.0	9.8	50.8	16.0	Satoh <i>et al.</i> , 2000
Sweden							12.5	Lie and Welander, 1997
Denmark	7.7	24.3	19.4			48.6		Henze <i>et al.</i> , 1987
Switzerland	11.4	31.8	11.4			45.4		Henze <i>et al.</i> , 1987
Hungary	8.5	28.6	20.0			42.8		Henze <i>et al.</i> , 1987
Germany	5.4	27.4	19.2			48.0	8.70	Makinia <i>et al.</i> , 2005
	11.5	19.3	9.60	48.1	11.5	59.6	7.60	Henze <i>et al.</i> , 1999
Japan	14.0*	14.0*	10.0*	54.0*	8.0*	62.0*	10.80*	Funamizu <i>et al.</i> , 1997
Denmark	3.0	29.0	11.0	43.0	14.0	57.0		Henze, 1992
Switzerland	10.0	16.0	9.0	40.0	25.0	65.0		Solfrank, 1988
France	7.9	57.3	10.5	21.0	3.5	24.5		Lesouef <i>et al.</i> , 1992
South-Africa	8.0	28.0	4.0			60.0		Ekama <i>et al.</i> , 1986
Netherlands	4.6	41.50	16.6			37.2	13.0	Vanveldhuizen <i>et al.</i> , 1999
Netherlands	6.6	31.8	19.00			42.5	9.80	Brdjanovic <i>et al.</i> , 1999
Average	8.7	28.9	12.9	41.2	12.0	49.5	11.10	

\* Estimate based on the article; \*\* Biomass COD is included in the slowly biodegradable substrate fraction

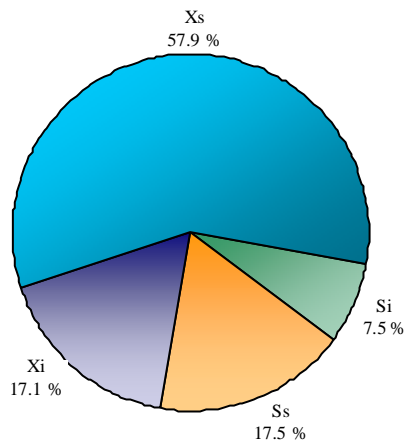


Fig. 2: Average COD fractions of raw sewage according to literature data

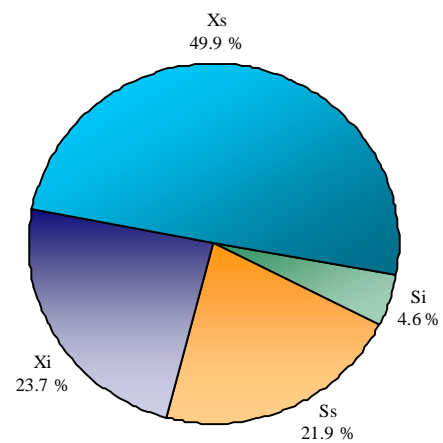


Fig. 3: Average COD fractions of raw wastewater based on Hungarian measurements

Table 3: COD fractions of Hungarian raw wastewater (experimental results)

WWTP	COD <sub>TOT</sub> (mg/L)	S <sub>I</sub> %	S <sub>S</sub> %	X <sub>I</sub> %	X <sub>S</sub> (+X <sub>H</sub> )**	VFA
Harskut	987.0	5.7	20.4	16.5	57.5	2.9
Liter	443.0	5.3	17.3	12.6	64.8	0.0
Nagyvazsony	765.0	3.3	20.0	29.4	47.3	7.1
Bakonybel	1092.0	2.4	27.3	32.5	37.9	
Borzavar	1362.0	3.2	26.8	22.1	48.0	
Dudar*	867.0	6.5	13.0	32.3	48.2	
Padrag	582.0	10.8	10.0	24.4	54.8	
Epleny	977.0	2.1	25.4	31.1	41.4	
Szapar	665.0	5.4	30.4	28.3	35.9	
Zirc*	280.0	3.9	10.1	20.6	65.5	
Veszprem	490.0	2.2	40.7	11.1	46.1	15.8
Min.	280.0	2.1	10.0	11.1	35.9	0
Max	1362.0	10.8	40.7	32.5	65.5	15.8
Max	773.6	4.6	21.9	23.7	49.8	6.5

\* Data validated by simulation; \*\* Biomass COD is included in the slowly biodegradable substrate fraction

of some countries. For example, Dutch wastewater contains high  $X_I$ , Swiss sewage has high  $S_I$  and Hungarian wastewater has low  $S_I$  ratio. However, such generalization is not warranted with scanty data. The high  $X_I$  can be explained as due to the long hydraulic residence time in sewage pipelines where a significant portion of the substrate fraction, biologically degraded, increases the ratio of inert particulate components. Outstanding inert soluble COD fraction in the sewage of large developed cities may be the result of industrial wastewater discharges. The differences between primary and raw wastewater COD fractions are along the expected lines; the soluble fractions ( $S_I + S_S$ ) in primary sewage are higher while particulate fractions ( $X_S + X_I$ ) are lower than in raw wastewaters. However, the decrement of suspended fraction and the increment of soluble fraction after clarification were very little that is only 12.5 %. The total substrate fraction ( $X_S + S_S$ ) is 3 % higher in primary wastewater than in raw sewage. This implies that the settling properties of biodegradable fractions are worse than those of the inert components. This is because the slowly biodegradable substrate ( $X_S$ ) has always some unabsorbed colloidal fraction that can not be settled in the primary clarifier. The Hungarian wastewater samples had, on the average 8 % lower  $X_S$  and 6.6 % higher  $X_I$  than the corresponding averages of literature data and this may result in increasing the aeration needs and sludge production of the WWTP (Figs. 2 and 3). However, the most interesting result is the relatively low (4.6 %) inert soluble fraction of the Hungarian samples as compared to the average of 7.5 % in the literature. If the influent total COD concentration in Hungarian wastewater is above 1000 mg/L (typical in Hungarian rural areas), then the WWTPs may have

difficulties to achieve the desired discharge limits (e.g.: 50 mg/L) in spite of the relatively low inert soluble fraction.

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