J. Chem. Tech. Biotechnol. 1997, **68**, 283–293

COD Fractionation in Wastewater Characterization—The State of the Art

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(Received 24 May 1996; revised version received 6 August 1996; accepted 15 August 1996)

Abstract: Wastewater characterization is now regarded as an indispensable step yielding all the necessary information for a reliable modelling and design of biological treatment processes. It should mainly include fractionation of the chemical oxygen demand (COD), and assessment of significant kinetic and stoichiometric coefficients. COD fractionation involves identification of inert and biodegradable COD together with readily biodegradable and slowly biodegradable fractions. Experimental methods developed or selected for the assessment of COD fractions should be compatible with the mathematical models defining biological treatment and should yield consistent and reliable values. A critical review of available experimental methodology is provided and values of significant COD components determined in this work and reported in the literature, for different types of domestic and industrial wastewaters are outlined.

Key words: wastewater characterization, COD fractionation, soluble inert COD, particulate inert COD, residual microbial products, readily biodegradable COD, slowly biodegradable COD

NOTATION

b_H	Endogenous decay rate (day^{-1})
BOD	Biological oxygen demand (mg COD dm^{-3})
COD	Chemical oxygen demand (mg COD dm^{-3})
C_{I1}	Total non-biodegradable COD (mg COD dm^{-3})
C_{S1}	Total biodegradable COD (mg COD dm^{-3})
C_{T1}	Total influent COD (mg COD dm^{-3})
f_{EX}	Inert fraction of biomass
f_{SS}	Readily biodegradable fraction
K_h	Hydrolysis rate contant (day^{-1})
MLVSS	Volatile suspended solids in the mixed liquor (mg VSS dm^{-3})
NO_2-N	Nitrite-nitrogen (mg N dm^{-3})
NO_3-N	Nitrate-nitrogen (mg N dm^{-3})
N_{OX}-N	Oxidized nitrogen (mg N dm^{-3})
ΔN_1	Amount of nitrogen acceptor consumed by growth on readily biodegradable substrate (mg N dm^{-3})
ΔO_2	Amount of oxygen consumption per unit volume (mg dm^{-3})
OUR	Oxygen uptake rate (mg dm^{-3} h^{-1})
S_{A1}	Fermentation products (mg COD dm^{-3})
S_{F1}	Fermentable readily biodegradable COD (mg COD dm^{-3})
S_{H1}	Influent rapidly hydrolysable COD (mg COD dm^{-3})
S_H	Effluent rapidly hydrolysable COD (mg COD dm^{-3})
S_{I1}	Influent soluble inert COD (mg COD dm^{-3})
S_P	Soluble residual COD generated as metabolic products (mg COD dm^{-3})
S_R	Effluent soluble residual COD (mg COD dm^{-3})
S_S	Effluent readily biodegradable COD (mg COD dm^{-3})
S_{S1}	Influent readily biodegradable COD (mg COD dm^{-3})
S_T	Effluent soluble COD (mg COD dm^{-3})
S_{T1}	Influent soluble COD (mg COD dm^{-3})
SS	Suspended solids (mg SS dm^{-3})
X_H	Active heterotrophic biomass (mg COD dm^{-3})

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J. Chem. Tech. Biotechnol. 0268-2575/97/$09.00 © 1997 SCI. Printed in Great Britain

X_{I1}	Influent particulate inert COD (mg COD dm^{-3})
X_P	Particulate inert metabolic products (mg COD dm^{-3})
X_{S1}	Influent slowly biodegradable COD (mg COD dm^{-3})
X_{T1}	Total influent particulate COD (mg COD dm^{-3})
VSS	Volatile suspended solids (mg VSS dm^{-3})
Y_H	Heterotrophic yield coefficient (mg cell COD (mg COD)$^{-1}$)
Y_{SP}	Ratio between the soluble residual products and initial COD
η_g, η_h	Correction factors for growth and hydrolysis under anoxic conditions
θ_X	Sludge age (day^{-1})
$\hat{\mu}_H$	Maximum specific growth rate for heterotrophs (day^{-1})
$\hat{\mu}_A$	Maximum specific growth rate for autotrophs (day^{-1})

1 INTRODUCTION

Modelling is a valuable tool for design of activated sludge systems, because it enables the role and impact of significant parameters to be analysed and so helps to define and optimize the proposed process. In this context, the value of modelling depends upon the accuracy and reliability of available experimental information, the wastewater to be treated and the biochemical reactions involved. Experimentally-derived information has to cover various wastewater fractions included as model components, biomass in activated sludge and wastewater and finally, various kinetic and stoichiometric coefficients defining the biochemical processes included in the model.

The identification of wastewater characteristics with regard to the organic content is useful both from the standpoint of process kinetics and prediction of effluent quality. Difficulties associated with the correct assessment of organic substrate have caused inconvenience and confusion, to the extent of hindering the progress of activated sludge theory. Collective analytical parameters such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD), routinely used to reflect the total organics in wastewaters, do not correspond to the real system variable, i.e. the growth limiting substrate. COD is estimated to be a more useful parameter than BOD as it enables one to make appropriate correlations among substrate, biomass and dissolved oxygen in terms of electron equivalence. It cannot, however, identify the growth limiting components directly related to the corresponding process rate expressions, especially in complex media such as domestic and industrial wastewaters.

From a modelling standpoint, COD cannot differentiate between biodegradable and inert organic matter or between readily and slowly biodegradable fractions. The inert COD may be present in the influent or it may be generated during biological treatment as residual microbial products. This residual COD fraction, not so critical for conventional wastes, becomes significant for industrial effluents and especially in strong wastes as it leads to misinterpretation of the biological treatability and kinetic analysis; the soluble inert COD fraction also becomes a challenging factor in meeting the effluent limitations expressed in terms of COD for a number of industrial categories.

Current understanding of activated sludge modelling for carbon and nitrogen removal involves a number of kinetic and stoichiometric coefficients, excluding parameters related to biological phosphorus removal. A significant proportion of these coefficients are defined for specific functions in the models and, therefore, are not sensitive to wastewater characteristics. A smaller group however, including maximum heterotrophic and autotrophic growth rates, $\hat{\mu}_H$ and $\hat{\mu}_A$, heterotrophic yield, Y_H, hydrolysis rate constant, K_h, and correction factors for anoxic conditions, η_g and η_h, are very much site specific and need to be experimentally determined for each case.

The paper is limited to a review of the significant methodology so far proposed for COD fractionation and the representative values associated with significant COD fractions for different types of domestic and industrial wastewaters.

2 COD FRACTIONATION

The COD parameter embodies different forms of organic carbon that require further differentiation in terms of their biodegradation characteristics. In this context, the total influent COD, C_{T1}, has two major components: the total non-biodegradable or inert COD, C_{I1}, and the total biodegradable COD, C_{S1}. The inert fraction may be further subdivided into soluble inert COD, S_{I1}, and particulate inert COD, X_{I1}. The soluble inert COD concentration in the influent bypasses the system without affecting the biochemical reactions in the reactor, whereas the particulate inert COD is entrapped and accumulated in the activated sludge and leaves the system through the sludge wastage stream.

The subdivision of the biodegradable COD originally relates to the bi-substrate model of Dold and Marais,[1] which identified two major fractions: readily biodegradable COD, S_{S1}, and slowly biodegradable COD, X_{S1}. The differentiation was based upon experimental observations showing a significant difference of approximately an order of magnitude between the rates of biodegradation of the two fractions. Evidently, each fraction contained a number of compounds associated with a range of biodegradation rates, but this range was estimated to be small compared with the rate difference between the two groups.[2] Recently, the readily biodegradable COD was further subdivided into fermentable readily biodegradable COD, S_{F1}, and fermentation products, S_{A1}, considered to be acetate, but in fact covering a whole range of other fermentation products.[3] This new subdivision was mainly proposed for mathematical modelling of biological phosphorus removal. The slowly biodegradable fraction, originally defined as particulate organics in the model proposed by Dold and Marais,[1] is now found to cover a wide range of particle size distribution from soluble to colloidal and larger organic particles of complex structure. The common feature of the particulate organics is that they cannot pass through cell wall and need to undergo extracellular hydrolysis prior to adsorption. Hydrolysis is advocated as the rate limiting step for the utilization rate of the slowly biodegradable organic matter. It may be difficult to characterize this fraction by a single value for the hydrolysis rate, since it exhibits a significant variation for various compounds in wastewaters. This argument provides the basis of the recent approach to subdivide this group into further fractions, namely rapidly hydrolysable COD, S_{H1}, and slowly hydrolysable COD, X_{S1}.[4] Figure 1 gives a schematical description of different wastewater COD fractions.

The mixed liquor and the process effluent exhibit a different COD structure from the wastewater. As far as soluble compounds are concerned, the quality of the process effluent is accepted to be the same as that of the mixed liquor, since process modelling generally includes the assumption that no biological activity takes place in the settling phase. The total effluent soluble COD, S_T, includes the non-biodegradable organics originating from the wastewater and by-passing the reactor, S_{I1}, a small portion of the biodegradable COD remaining after biological oxidation ($S_S + S_H$), and soluble residual COD generated as metabolic products, S_P (Fig. 2(a)). Consequently, the effluent stream generally contains more soluble inert COD than the wastewater, since the effluent soluble residual COD, S_R, includes soluble residual products aside from the soluble inert COD of the wastewater by-passing the reactor.

$$S_R = S_{I1} + S_P \qquad (1)$$

The generation of the soluble inert products have been incorporated into mathematical models by means of growth-associated or decay-associated processes.[5] In the models where soluble inert products are not included as a separate component, the entire residual COD, S_R, is measured and considered as a fictitious influent inert COD concentration.

Similarly, the particulate COD in the mixed liquor and the process effluent has four fractions (Fig. 2(b)). The major component is the active biomass, X_{H1}, that is sustained in the reactor using the biodegradable COD as the energy and carbon source. The other component may be a small fraction of the particulate slowly biodegradable organics, X_{S1}, remaining after hydrolysis and subsequent utilization. The mixed liquor also contains particulate inert COD of wastewater origin, X_{I1}, that is enmeshed in the sludge and accumulated in the reactor. This is not the only particulate non-biodegradable COD fraction: particulate inert organic products, X_P, are generated as a result of the microbial metabolic activity, during the endogenous decay or the death-regeneration phase, depending on the type of model

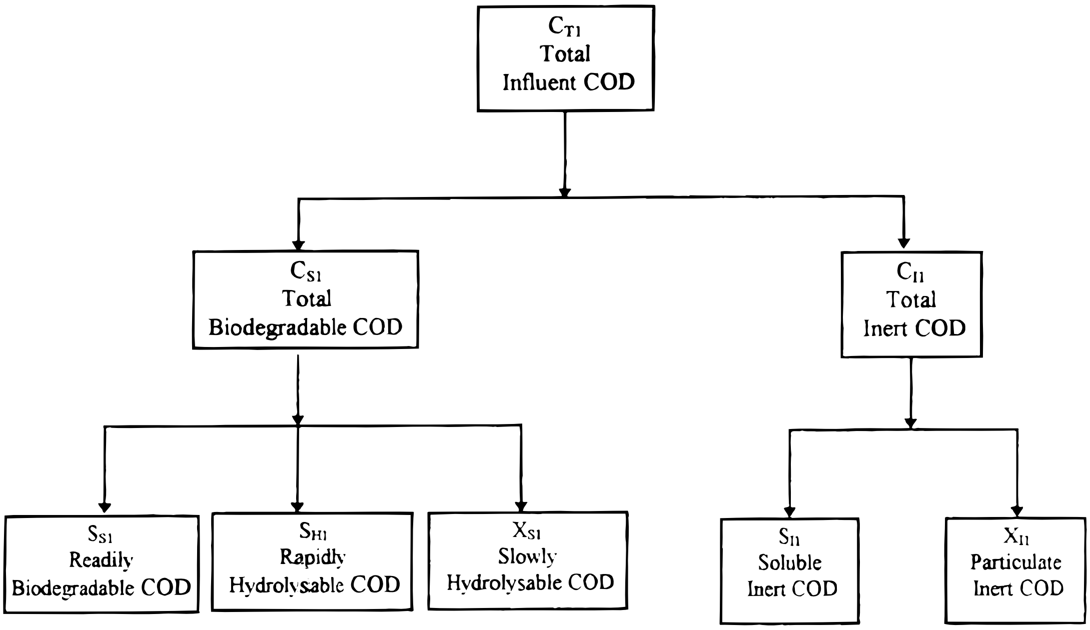

Fig. 1. Distribution of COD fractions in wastewaters.

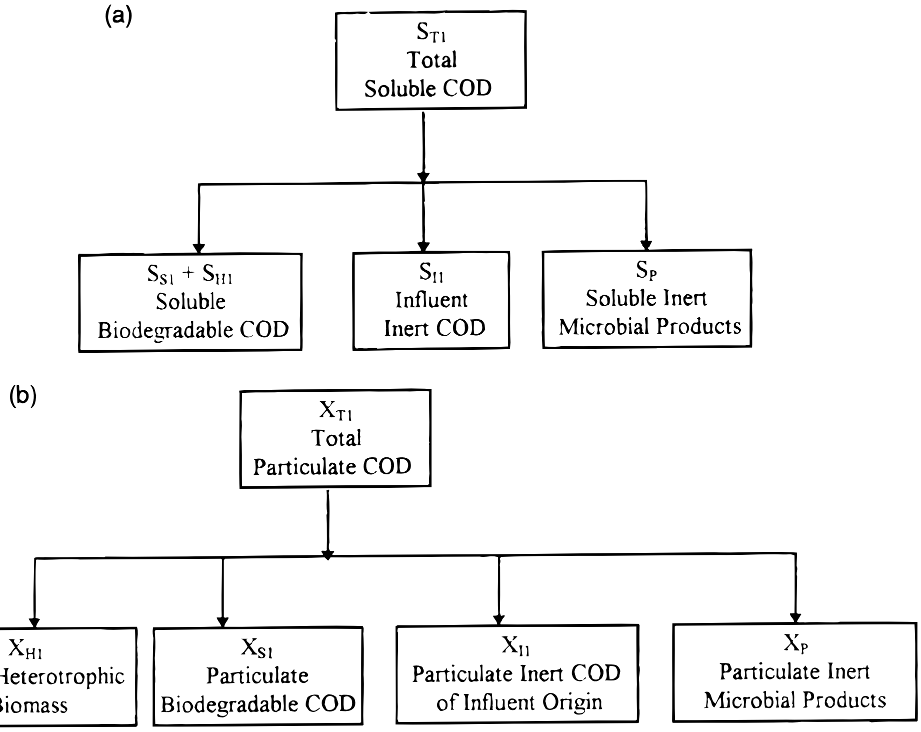

Fig. 2. COD fractions in the mixed liquor: (a) soluble COD components; (b) particulate COD components.

adopted. This spectrum accounts only for the organic structure of the activated sludge, also expressed in terms of the VSS parameter. The inorganic fraction of the activated sludge is also important in the process design, it is quantified as the difference between the mixed liquor suspended solids (SS), and volatile suspended solids (VSS), concentrations.

3 EXPERIMENTAL ASSESSMENT OF COD FRACTIONS

3.1 The readily biodegradable COD, S_{S1}

The readily biodegradable COD is presumably composed of soluble compounds such as volatile fatty acids, simple carbohydrates, alcohols, amino acids, etc. that can be directly absorbed for synthesis. In current mathematical models, the readily biodegradable COD concentration is conceived as the rate limiting component for heterotrophic growth. This component may be expressed as a fraction of the total COD:

$$S_{S1} = f_{SS} C_{T1} \tag{2}$$

where f_{SS} = readily biodegradable fraction of the influent COD.

All significant methods proposed for the determination of readily biodegradable organic matter rely on respirometric measurements conducted under aerobic or anoxic conditions, using continuous or batch reactors. Procedures involving other techniques, such as that of Mamais *et al.*[6] proposing settling and adsorption of organic compounds, other than the assumed readily biodegradable fraction, by physical–chemical methods, may yield empirical results, if they disregard the biochemical nature of the process. The aerobic batch test basically relies on observation of the oxygen uptake rate (OUR) a parameter indicating the amount of oxygen consumption per unit time, per unit reactor volume, due to microbial activities. The initial OUR is usually associated with the readily biodegradable substrate. Ekama *et al.*[7] claim that the initial OUR may stay constant over a period of 1–3 h where the readily biodegradable substrate, S_{S1}, is high enough to sustain maximum growth rate, if a suitable food to microorganism (F/M) ratio is selected. After the consumption of S_{S1}, OUR is expected to drop to a lower level only correlated with the hydrolysis of slowly biodegradable substrate and endogenous respiration. The readily biodegradable COD is sewage, S_{S1}, may be calculated from the following relationship:

$$S_{S1} = \frac{1}{1 - Y_H} \Delta O_2 \tag{3}$$

where ΔO_2 is the difference between total respiration and respiration due to hydrolysed substrate and endogenous metabolism and Y_H is the heterotrophic yield. The value of the yield coefficient, Y_H, may either be theoretically calculated for each type of wastewater, on the basis of the energetics of the process stochiometry,[8] or experimentally assessed using similar respirometric techniques.[9,10] For domestic sewage, a default value of 0·45 g VSS^{-1} g COD (or 0·64 g cell COD^{-1} g COD) is commonly used for this coefficient.[3]

If further subdivision of S_{S1} is required for the individual assessment of S_{F1} and S_{A1}, the latter has to be measured as the acetic acid or volatile acid concentration; then S_{F1} can be calculated as

$$S_{F1} = S_{S1} - S_{A1} \tag{4}$$

The same COD fraction may also be calculated from the oxidized nitrogen concentration profile in an anoxic reactor. In this test the initial electron acceptor utilization rate is faster, due to the oxidation of the readily biodegradable substrate, yielding the values of S_{S1} by means of the following expression:

$$S_{S1} = \frac{2{\cdot}86}{1 - Y_H} \Delta N_1 \tag{5}$$

An example of the observed OUR and NUR profiles for the assessment of the readily biodegradable COD fraction is given in Figs 3(a) and 3(b), illustrating the results of aerobic and anoxic batch tests conducted in this work[10] on Istanbul domestic sewage, under experimental conditions described by Ekama *et al.*[7] It should be noted that appropriate correction for the accumulation of NO_2-N is a prerequisite for an accurate evaluation of S_{S1} in the anoxic test. Table 1 summarizes average values of S_{S1} and f_{SS} experimentally determined for a number of domestic and industrial wastewaters.[11]

3.2 The inert COD fractions and residual microbial products

Assessment of the inert fraction of the organic matter is very important because it indicates indirectly the other main fraction, which is biodegradable organic matter, i.e. substrate available for microbial growth and electron acceptor utilization. A number of methods have so far been proposed for the estimation of inert fractions in wastewater, as listed in Table 2.[12]

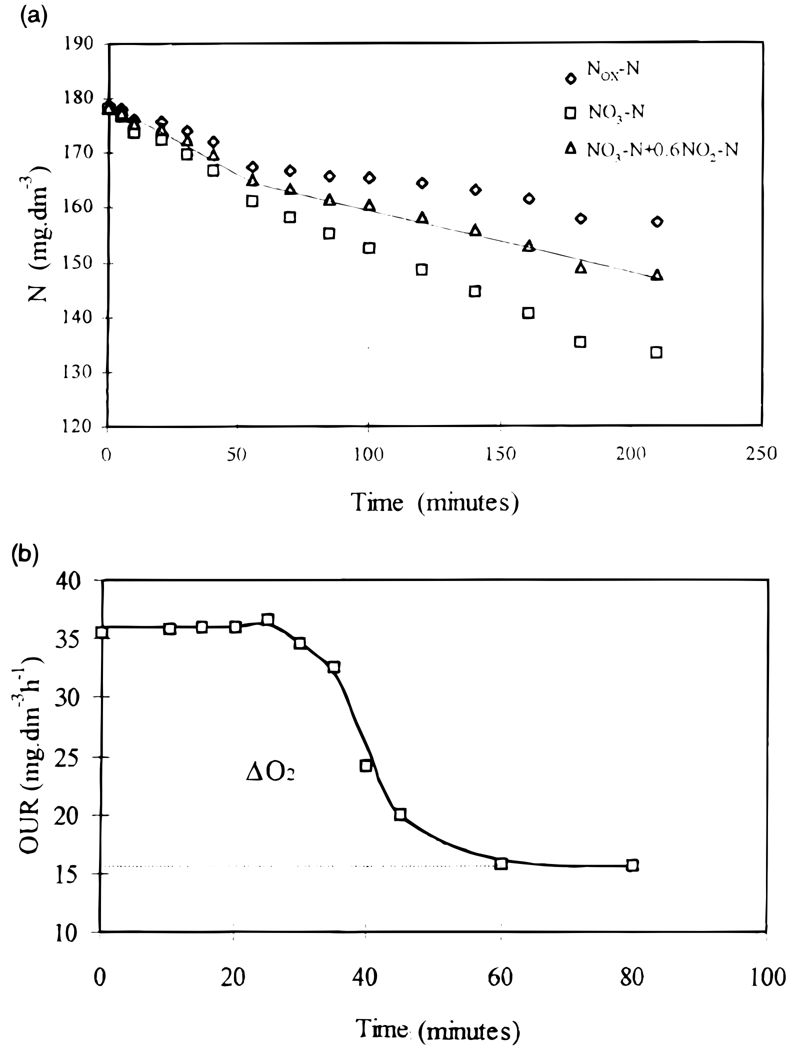

Fig. 3. (a) The NUR test for the assessment of the readily biodegradable COD in domestic sewage. (b) The OUR test for the assessment of the readily biodegradable COD in domestic sewage.

TABLE 1
Readily Biodegradable COD of Different Wastewaters[11]

Type of wastewater	C_{T1}(*mg dm*$^{-3}$)	S_{S1}(*mg dm*$^{-3}$)		f_{SS}	
		NUR	*OUR*	*NUR*	*OUR*
Domestic	566	50·5	50	0·091	0·088
Meat processing plant	2686	374	392	0·155	0·170
Dairy industry	1745	406	397	0·233	0·228
Confectionary	3790	720	710	0·189	0·187

The importance of the initial soluble inert organic matter, S_{I1}, is recognized in the literature.[13] Ekama *et al.*[7] suggested the use of a laboratory completely mixed reactor system operated at sludge ages, θ_X, between 10 and 20 days, and stipulated that the influent soluble inert organics will be equivalent to the COD of the filtered effluent. Later, the IAWPRC Task Group defined a different method which consisted of removing an aliquot from the mixed liquor from a continuously fed completely mixed reactor operated at a sludge age in excess of 10 days and aerating it in a batch reactor;[14] the final soluble residual COD determined by periodical sampling and analysis was assumed to be equal to the soluble inert COD concentration in the feed. These types of methods have the major drawback of not differentiating between soluble inerts in the effluent and soluble residual fraction of microbial products, and measuring them together. This simplified approach may be tolerated for domestic wastewaters provided that the existence of residual products are accounted for in the determination of other organic fractions. However, it is likely to cause serious problems in the characterization of strong industrial wastes.

The nature of the soluble microbial products is not well established. As outlined above, most studies claim that they are residual; others state that they are biodegradable, but at a much slower rate than the biodegradable COD in the influent stream, leading to their accumulation in the system. Experimental evidence may be used to postulate that a portion of the soluble microbial products undergo biodegradation at such a slow rate that they may be considered inert for the operating conditions of the activated sludge system. The formulation of the rate of their generation or accumulation depends on the way in which the sludge age is incorporated in the mathematical model adopted.[12]

Similarly, a significant research effort is devoted to the assessment of the initial particulate inert organics, X_{I1}. Procedures generally suggested for the assessment of this component involve the kinetic analysis of a laboratory-scale completely mixed activated sludge unit operated at steady-state with a θ_X value longer than 5 days: Ekama *et al.*[7] propose to calculate X_{I1} by comparing the measured MLVSS concentration with the calculated value on the basis of process kinetics. The Task Group recommends a similar approach based upon the comparison of observed and calculated sludge production. These procedures require that three kinetic constants, namely the heterotrophic yield, Y_H, the endogenous decay rate, b_H, and the inert fraction of the

TABLE 2
Methods for Estimating Inert Organic Fractions in Wastewater

Organic fraction	*Test methods*	*Reference*
Soluble inert organics	Batch	Chudoba[13]
	Continuous	Ekama *et al.*[7]
	Batch	Henze *et al.*[14]
	Batch	Boero *et al.*[15]
	Batch	Germirli *et al.*[16]
	Batch/continuous	Sollfrank *et al.*[17]
	Batch	Lesouef *et al.*[18]
	Batch	Germirli *et al.*[19]
Particulate inert organics	Continuous + model calculation	Ekama *et al.*[7]
	Calibrated with sludge production	Henze *et al.*[14]
	Batch	Orhon *et al.*[20]
	Batch	Kappeler & Gujer[21]
	Batch	Lesouef *et al.*[18]
	Batch	Germirli *et al.*[19]

TABLE 3
Experimental Results on Soluble Inert COD Fractions

Wastewater category	S_{T1} (*mg dm*$^{-3}$)	S_{I1} (*mg dm*$^{-3}$)	Y_{SP}	*Reference*
Municipal wastes				
Domestic	150	8	0·096	Orhon *et al.*[23]
	164	13	0·064	Orhon *et al.*[23]
	250	15	0·062	Lesouef *et al.*[18]
Municipal (Domestic—tanneries)	190	15	0·086	Orhon *et al.*[23]
Industrial Wastes				
Tannery	1500	323	0·040	Kabdaşh *et al.*[24]
	1075	262	0·040	Kabdaşh *et al.*[24]
	1870	464	0·045	Kabdaşh *et al.*[24]
Textile				
Woven fabric	1176	90	0·044	Orhon *et al.*[20]
Knit fabric	800	88	0·040	Orhon *et al.*[20]
Knit fabric	535	117	0·088	Orhon *et al.*[20]
Cotton and synthetics dying and finishing	1000	190	0·083	Orhon *et al.*[16]
Dairy				
Integrated	480	—	0·068	Orhon *et al.*[25]
Yogurt and buttermilk	1190	—	0·062	Orhon *et al.*[25]
Pulp and paper	3340	137	0·057	Germirli *et al.*[16]
Meat processing	1990	110	0·057	Germirli *et al.*[16]
Antiobiotics	9330	2520	0·100	Germirli *et al.*[16]
Strong wastes				
Cheese whey				
Anaerobic influent	60000	—	0·027	Germirli *et al.*[19]
Aerobic influent	1020	256	0·054	Germirli *et al.*[19]
Citric acid plant				
Anaerobic influent	29300	1870	0·054	Germirli *et al.*[19]
Aerobic influent	2025	804	0·210	Germirli *et al.*[19]
Anaerobic influent	28100	1600	0·060	Germirli *et al.*[19]
Aerobic influent	4055	1900	0·078	Germirli *et al.*[19]

biomass, f_{EX}, be correctly determined by independent experimental methods.

Recently a new procedure has been proposed, enabling direct experimental determination of the influent particulate and soluble inert fractions.[21,22] It only relies on COD measurements and eliminates the basic problems associated with the earlier approaches: (a) influent and generated soluble inert organics are separately identified and the interference of S_P on the assessment particulate inert organics is avoided; (b) other kinetic and stoichiometric coefficients such as Y_H, b_H and f_{EX} are not required. The procedure basically uses the principle that both soluble and particulate inert microbial products, S_P and X_P, can be expressed as a constant fraction of the influent biodegradable COD, C_{S1}. The experiment requires two aerated batch reactors, one started up with the unfiltered wastewater (C_{T1}) and the other with the filtered wastewater (S_{T1}). In each reactor, total and soluble COD are monitored for a period long enough to ensure the depletion of all biodegradable substrate and the mineralization of all biomass so that the measured C_{T1} and S_{T1} values reach their constant threshold levels containing only initial inert COD and residual products. Both reactors are initially seeded by a minimal amount of biomass previously acclimated to the wastewater to avoid the interference of residual COD released through the decay of the initial inoculation. It is suggested that the acclimation be carried out in fill and draw systems operated at F/M ratios over 1·0 g COD g^{-1} VSS day^{-1} to ensure a highly viable biomass, and the amount of seed is adjusted between 10 and 50 mg dm^{-3}, depending on the nature of the wastewater to be tested.

The previous method for the assessment of S_{I1} is applicable to wastewater samples with a reasonable large particulate COD fraction. This component may be too small or practically negligible in some industrial wastewaters or in the effluent from the chemical treatment step of multi-stage treatment schemes commonly used for complex strong wastes. For such wastes, the procedure proposed by Germirli *et al.*[16] may be followed; it also consists of running two parallel aerated batch reactors of filtered wastewater and glucose, seeded with a very small amount of biomass previously acclimated to the glucose–wastewater mixture. Glucose is selected because it is the central compound of vital importance which appears in the metabolic pathways of the biodegradation of every organic matter. At the end of the experiment where all biodegradable substrates in the two reactors are depleted, the difference between the residual COD levels may be manipulated to yield the initial inert COD in the wastewater tested and the ratio between the soluble residual products and the initial COD, Y_{SP}.

Experimental results related to soluble and particulate inert COD fractions in wastewaters are outlined in Tables 3 and 4. Evaluation of the data presented in Table 3 should take into account that the effluent quality is significantly affected by the inert fraction of the influent COD as well as the generation of residual microbial products. It should be noted that the total residual effluent COD for such industries as tannery, textile, pulp and paper, etc. requires that effluent limitations be reviewed if biological processes are to be maintained as appropriate treatment technologies. This is especially true for industries producing strong wastes, as illustrated in Table 3.

3.3 The slowly biodegradable COD fractions

Slowly biodegradable organic fractions, X_{S1}, are generally determined from mass balance. In models where slowly biodegradable CODs is not further differentiated as rapidly and slowly hydrolysable components, and initial biomass is not separately identified, the following mass balance yields X_{S1}, provided that S_{S1} is experimentally estimated.

$$C_{S1} = S_{S1} + X_{S1} \tag{6}$$

Rapidly hydrolysable COD, if considered as a model component, is generally assumed to be predominantly soluble, so that it may be defined with a reasonable approximation for domestic wastewaters by means of the mass balance expression below:

$$S_{H1} = S_{T1} - S_{I1} - S_{S1} \tag{7}$$

A similar mass balance on the particulate COD fractions may be used to calculate the slowly hydrolysable COD.

3.4 COD fractionation of different wastewaters

Results of extensive experimental work,[10] carried out on COD fractionation of a wide range or domestic and industrial wastewaters are given in Table 5. Experiments were conducted on raw samples, since the resulting data were expected to reflect the character of the wastewaters investigator. The COD fractionation data on Istanbul domestic sewage, presented above, may be compared with similar results outlined in Table 6, reported for the same type of wastwater in different parts of the world. The two sets of data in Tables 5 and 6 support the general consensus that sewage quality and structure are site-specific and should be determined individually for each case. An evaluation for the COD fractionation of industrial wastewaters is not possible as there are no similar data available in the literature. The

TABLE 4
Experimental Results on Particulate Inert COD Fractions

Wastewater category	C_{T1} (*mg dm*$^{-3}$)	X_{I1} (*mg dm*$^{-3}$)	*Reference*
Municipal wastes			
Domestic	314	29	Orhon *et al.*[23]
	360	36	Orhon *et al.*[23]
	440	30	Lesouef *et al.*[18]
Municipal (Domestic—tanneries)	390	112	Orhon *et al.*[23]
Industrial wastes			
Textile			
Knit fabric	535	73	Orhon *et al.*[20]
Strong wastes			
Cheese whey			
Aerobic influent	2761	28	Germirli *et al.*[19]
Citric acid plant			
Aerobic influent	2945	228	Germirli *et al.*[19]

TABLE 5
Experimental Results on Distribution COD Fractions of Different Wastewaters (mg dm^{-3})[10]

Wastewater	C_{T1}	S_{T1}	X_{T1}	S_{S1}	S_{I1}	X_{I1}	S_{H1}	X_{S1}	S_{S1}/C_{T1}	S_{S1}/S_{T1}	S_{I1}/C_{T1}	S_{I1}/S_{T1}	S_{H1}/C_{T1}	S_{H1}/S_{T1}	X_{S1}/C_{T1}	X_{I1}/C_{T1}
Domestic	315	150	165	40	20	42	90	123	0·127	0·267	0·063	0·133	0·286	0·600	0·390	0·133
	670	185	485	61	18	52	106	433	0·091	0·329	0·027	0·097	0·158	0·573	0·646	0·078
	585	150	435	75	16	60	59	375	0·128	0·500	0·027	0·107	0·101	0·393	0·641	0·103
Çirağan Hotel	630	370	260	40	56	63	174	197	0·222	0·378	0·089	0·151	0·276	0·470	0·313	0·100
Confectionary	3380	3120	260	735	77	—	2308	260	0·217	0·236	0·023	0·025	0·683	0·740	0·077	—
	3000	2500	500	2045	45	—	410	500	0·682	0·818	0·015	0·018	0·137	0·164	0·167	—
	1800	1495	305	840	105	—	550	305	0·470	0·562	0·058	0·070	0·306	0·368	0·169	—
	8085	6775	1310	5370	45	—	1360	1400	0·664	0·793	0·006	0·007	0·1682	0·201	0·173	—
Dairy	1410	1075	335	400	—	105	675	230	0·284	0·372	—	—	0·479	0·628	0·163	0·074
Tannery	2410	1210	1200	300	140	265	770	935	0·124	0·248	0·058	0·116	0·319	0·636	0·388	0·110
	—	775[a]	—	230	120	—	425	—	—	0·298	—	0·155	—	0·548	—	—
	—	1080[a]	—	340	200	—	540	—	—	0·315	—	0·185	—	0·500	—	—
Textile	935	470	465	135	12	188	323	277	0·144	0·287	0·013	0·026	0·345	0·687	0·296	0·201
	785	560	225	152	21	45	387	180	0·194	0·271	0·027	0·038	0·495	0·691	0·229	0·057
Meat	2600	1140	1460	380	30	305	730	1155	0·146	0·333	0·012	0·026	0·281	0·640	0·444	0·117

[a] Chemical treatment effluent.

TABLE 6
Reported COD Fractionation Results for Domestic Wastewaters.

	C_{T1} *or* C_{TS1} (*mg* dm^{-3})	S_{I1} (%)	S_{S1} (%)	X_{S1} (%)	X_{H1} (%)	X_{I1} (%)	*Reference* (%)
Raw							
South Africa	530	5	20	62	—	13	Ekama *et al.*[7]
Denmark	—	2	20	40	20	18	Henze *et al.*[26]
Primary							
South Africa	370	8	28	60	—	4	Ekama *et al.*[7]
Switzerland	220	11	32	45	—	11	Henze *et al.*[14]
Hungary	350	9	29	43	—	20	Henze *et al.*[14]
Denmark I	515	8	24	49	—	19	Henze *et al.*[14]
Denmark	—	3	20	43	14	11	Henze *et al.*[26]
Switzerland I	250	20	11	53	7	9	Kappeler & Gujer[21]
Switzerland II	430	10	7	60	15	8	Kappeler & Gujer[21]
Switzerland III	325	12	8	55	15	10	Kappeler & Gujer[21]
Switzerland IV	190	8	10	56	—	26	Siegrist *et al.*[27]
Switzerland V	250	8	10	58	—	24	Siegrist *et al.*[27]
Switzerland VI	360	10	16	40	25	9	Sollfrank *et al.*[28]
Spain I	340	9	18	33	15	25	de la Sota *et al.*[29]
France I	450	10	33	44	—	13	Lesouef *et al.*[18]
France II	345	6	25	41	—		Lesouef *et al.*[18]

results show clearly that the total organic content characterized by the total COD concentration, C_{T1}, gives inadequate, if not misleading information about the biological treatability of different wastewaters. Confectionary wastes for example, having a total COD concentration of over 3000 mg dm^{-3}, appear to be more easily amenable to biological treatment than textile, leather or meat processing wastewaters as their major COD fraction is readily biodegradable.

Another common and significant feature of experimental observations is the fact that the slowly biodegradable COD should be considered as the major rate limiting process component for heterotrophic growth in biological treatment systems. In fact, in the conventional kinetic approach, the entire BOD or the COD concentration in the wastewater is conceived as the rate limiting substrate in heterotrophic growth. With the introduction of COD fractionation, this approach is totally abandoned in the new models which now state that heterotrophic growth is controlled alone by the readily biodegradable substrate which is either present in the wastewater, or generated through the hydrolysis of slowly biodegradable organic matter.[3,12] As clearly shown in this paper, the initial readily biodegradable COD is a relatively small fraction of the total COD content of wastewaters. Therefore, biological treatment systems are not controlled by the depletion of the readily biodegradable organics, but by hydrolysis of slowly biodegradable organics, a much slower process compared with heterotrophic growth. Consequently, appropriate design of biological treatment, especially for industrial wastewaters, and the assurance of the desired effluent quality should solely account for the hydrolysis or organics, a factor entirely overlooked in conventional practice.

Another issue of practical significance is the problem created by more and more stringent COD criteria, imposed as effluent limitations for domestic and industrial wastewaters, with the belief that they can be met with biological treatment at longer hydraulic retention times and higher sludge ages. The COD fractionation data presented in this paper provide clear evidence that such limitations cannot be achieved, due to inert COD fractions of wastewaters. They further indicate that the effluent quality with respect to soluble organics, is likely to deteriorate at higher sludge ages with the accumulation of residual metabolic products.[5]

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