Wat. Sci. Tech. Vol. 26, No. 3-4, pp. 815–825, 1992.
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0273–1223/92 $15.00

THE EFFECT OF RESIDUAL COD ON THE BIOLOGICAL TREATABILITY OF TEXTILE WASTEWATERS

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ABSTRACT

Textile effluents often contain an array of chemicals with different biodegradation characteristics. Consequently, it is quite difficult to evaluate and interpret the degree of COD removal that can be attained by biological treatment without identifying COD portions that are resistant to biodegradation. This study evaluates the biological treatability of textile wastewaters generated by the knit and wowen fabric finishing category with specific emphasis on the assessment of different residual COD components. A new method is proposed to experimentally measure the initial particulate inert COD. The method is tested to yield a value of 73 mgl^{-1} for this COD component, corresponding to 16 % of the particulate COD in the textile sample. A previously developed procedure is used to quantify the initial soluble inert COD and the residual COD generated through microbial metabolism during the treatment process. The ratio of the inert fraction to the soluble COD of the textile effluents is found to vary between 0.076 and 0.22. A similar ratio in the range of 0.04 – 0.09 is calculated for the residual microbial products. The kinetic and stoichiometric constants associated with the biodegradable COD are also experimentally measured. The residual components, together with the kinetic information about biodegradable fractions, are used to simulate the performance of activated sludge systems by means of a relationship between the total effluent COD and the sludge age. The results indicate that the residual components practically dominate the effluent COD and seriously challenge related effluent standards.

KEYWORDS

Activated sludge; process kinetics; textile wastewaters; initial particulate inert COD; initial soluble inert COD; residual soluble microbial products; kinetic and stoichiometric constants.

INTRODUCTION

Textile industry involves a complex sequence of production and finishing technologies. This complexity is often reflected in the structure of its wastewater, usually containing high but variable concentrations of BOD and COD together with a number of priority pollutants. In a number of countries, effluent emissions standards expressed on a concentration basis are implemented. In Turkey, effluent limits, in the range of 40 - 100 mgl^{-1} for BOD, and 200 - 300 mgl^{-1} for COD, are in use for different categories of the textile industries requiring removal efficiencies of around 80-90% for these parameters. Chemical treatment, generally considered as one of the alternative processes, is observed to provide highly fluctuating BOD and COD removal efficiencies (Germirli *et al.*, 1990). This observation is quite reasonable since chemical separation and precipitation depend upon a number of different factors such as type of dye, fabric, etc., showing significant variations in an operating sequence, even in the same plant. Therefore chemical treatment alone does not prove reliable and biological treatment is inevitably prescibed to ensure consistent removal efficiences yielding an effluent quality below the regulatory limits. While this is often achieved for BOD, adequate COD removals require a careful evaluation of the structural characteristics of this parameter with respect to various components it defines on an overall basis. In fact, textile wastewaters are generally characterized by a multitude of chemicals from different steps of the plant operation, mainly dyeing and finishing processes. They all contribute to the wastewater COD at different levels. There is substantial evidence in the literature to show that a portion of these chemicals are resistent to biodegradation under regular conditions: A recent study indicated that only 47 % of the dyestuffs commonly used in the textile operation are biodegradable (Pagga and Brown, 1986). Consequently the magnitude of non-biodegradable components in a textile wastewater plays a decisive role in assessing the capabilities and limitations of biological treatment.

In this study, the effect of non-biodegradable COD components on the biological treatability of textile wastewaters was experimentally investigated. In this context, samples from three different textile wastewaters, one belonging to the wowen fabric finishing and the others to the knit fabric finishing categories, were studied to yield the following: (a) the initial soluble inert COD fraction, (b) the rate of soluble residual COD generation through microbial activities, (c) the initial particulate inert COD, (d) the kinetic and stoichiometric parameters related to the biodegradable COD. The residual COD components, together with pertinent information related to the biodegradable COD, are processed to yield a relationship between total effluent COD attainable by biological treatment and the sludge age of the treatment process.

The paper also describes and uses a new method for the direct experimental assessment of the particulate inert COD which could be previously quantified only by curve fitting methods (Henze *et al.*, 1987).

CONCEPTUAL APPROACH

The best way to evaluate biological treatability is to adopt a rational description of the process based on applicable microbial growth kinetics and continuity expressions. The major drawback of this approach as well as other evaluation methods is the limitation imposed by the available substrate parameters, such as BOD, COD, TOC; COD, often described as the best substrate parameter from the process kinetics standpoint, does not differentiate between biodegradable and residual components. This limitation is totally reflected in the traditional process modelling, which regards influent COD as an overall parameter subject to biodegradation by a single set of kinetic and stoichiometric coefficients. Consequently, it postulates that the effluent COD is solely composed of the remaining fraction of the influent COD which then may be reduced to practically zero by increasing the sludge age. While this assumption may be tolerated for domestic wastewaters, it may lead to severe conceptual errors of practical significance for industrial wastewaters and especially textile effluents containing appreciable amounts of non-biodegradable COD components.

From a structural viewpoint, the limitations of the traditional models may be attributed to the fact that they are formulated for the overall substrate and biomass parameters only and for two processes, namely bacterial growth and decay. Recently this approach was expanded (Henze *et al.*, 1987) and modified (Orhon *et al.*, 1989; Artan *et al.*, 1990) to include eight components and three processes for carbonaceous compounds. Aside from the degradable soluble substrate, S_S and the dissolved oxygen, S_0, the initial soluble inert COD, S_I and soluble residual microbial products, S_P are defined as soluble components; four particulate components include active biomass, X_A, slowly degradable particulate matter X_S, particulate inert products, X_P and initial particulate inert COD, X_I. The new modelling approach enables the derivation of the following expressions to describe the performance of activated sludge systems operated at steady-state (Artan *et al.*, 1990; Orhon *et al.*, 1991).

$$-\frac{\hat{\mu}}{Y}\frac{S_S}{K_S + S_S}X_A + KX_S - D_H S_S = -D_H S_{S0} \tag{1}$$

$$(1 - f_P)b_H X_A - KX_S - D_X X_S = -D_H X_{S0} \tag{2}$$

$$\hat{\mu}\frac{S_S}{K_S + S_S}X_A - b_H X_A - D_X X_A = 0 \tag{3}$$

$$f_P b_H X_A - D_X X_P = 0 \tag{4}$$

$$\alpha\hat{\mu}\frac{S_S}{K_S + S_S}X_A - D_H S_P = 0 \tag{5}$$

In the above expressions, the generation of soluble residual microbial products, S_P is defined as a growth-associated mechanism by means of a rate coefficient α. These expressions do not include initial inert components S_I and X_I as they do not participate in any of the biochemical conversion processes and therefore by-pass the treatment system.

A New Method for the Determination of initial Particulate Inert COD

Utilization of the new modelling approach by means of continuity equations 1 to 5, with respect to inert COD components, is only possible if S_I and X_I are experimentally determined and if the rate coefficient, α related to S_P is then calculated.

The basis of the proposed experimental approach relies on the justifiable hypothesis that S_P is always proportional to the total degradable COD depleted at any given time. This hypothesis may be varified as follows:

From equation 2, X_S may be defined as;

$$X_S = \frac{(1 - f_P)b_H X_A + D_H X_{S0}}{K + D_X} \tag{6}$$

Substituting the above expression and considering $D_X \ll K$, equation 1 may be arranged to yield;

$$\frac{X_A}{D_H} = \frac{Y(C_{S0} - S_S)}{D_X + ab_H} \tag{7}$$

where C_{S0} is the initial total biodegradable COD;

$$C_{S0} = X_{S0} + S_{S0}$$

and

$$a = 1 - Y(1 - f_P)$$

From equation 5;

$$S_P = a(D_X + b_H)\frac{X_A}{D_H} \qquad (8)$$

Substituting X_A/D_H from 7 into the above expression, S_P may be redefined as;

$$S_P = \frac{aY(D_X + b_H)}{D_X + ab_H}(C_{S0} - S_S) \qquad (9)$$

In case of an experimental study long enough for $\Theta_X \approx \infty$ where $S_S \approx 0$

$$\lim_{\theta_x \to \infty} S_P = \lim_{D_x \to 0} S_P = a\frac{Y}{1 - Y(1 - f_P)}C_{S0} \qquad (10)$$

or

$$S_P = Y_P\, C_{S0} \qquad (11)$$

where

$$Y_P = \alpha\frac{Y}{1 - Y(1 - f_P)} \qquad (12)$$

Y_P can easily be calculated from experimental setups outlined below and be used to calculate the rate coefficient α,

$$\alpha = \frac{Y_P[1 - Y(1 - f_P)]}{Y} \qquad (13)$$

In this context, the experimental method for the determination of X_I is developed as a modification of the one previously proposed by Germirli *et al.*, (1991) to assess S_I. Basically, the method involves running three batch reactors, two with the wastewater to be tested and the third with glucose. The first one of the wastewater reactors is started with the total COD, C_{T0}, and the second with the total soluble COD, S_{T0}, whereas the initial COD in the glucose reactor is adjusted to equal S_{T0}. In the reactors, the change in the soluble COD profiles is observed and the test is continued for a period enough to entirely deplete the degradable COD. As schematically shown in Fig. 1, the soluble COD in the glucose reactor reaches a level characterizing S_{PG} alone, as glucose contains no initially inert fraction as a pure compound; in the wastewater reactor started with S_{T0}, it is reduced to a minimum level S_{R1} equal to the sum of S_I and S_{P1}. Consequently, S_I fraction in the wastewater can be computed as;

$$S_I = S_{R1} - S_{PG} \qquad (14)$$

with the assumption that;

$$(S_P)_{\text{wastewater}} \approx (S_P)_{\text{glucose}}$$

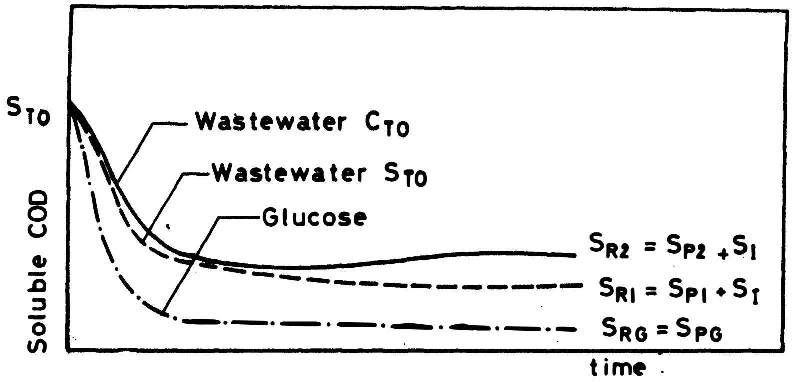


Fig. 1. Experimental evaluation X_I

This assumption is justifiable as the two reactors are operated approximately with the same S_{S0}; S_I may be correlated to S_{T0} with a coefficient, Y_I ;

$$Y_I = \frac{S_I}{S_{S0}} \tag{15}$$

A similar stoichiometric correlation may be established for S_P with the previously defined Y_P:

$$Y_P = \frac{S_{R1} - S_I}{S_{T0} - S_I} = \frac{S_{P1}}{S_{S0}} \tag{16}$$

The reactor started with both soluble and particulate degradable fractions of the wastewater will exhibit a higher residual soluble COD, S_{R2} due to a higher S_{P2}. As S_I is determined as mentioned above

$$S_{P2} = S_{R2} - S_I \tag{17}$$

From expression 11;

$$C_{S0} = \frac{S_{P2}}{S_{P1}} S_{S0} \tag{18}$$

and

$$X_I = C_{T0} - C_{S0} - S_I \tag{19}$$

This way, the proposed method enables us to experimentally assess the four COD components in the wastewater sample tested, namely X_I, X_{S0}, S_{S0} and S_I together with stoichiometric constants Y_I and Y_P, and it allows us to compute α defining the generation rate of soluble residual microbial products, S_P.

EXPERIMENTAL APPROACH AND RESULTS

The experiments were conducted on effluents of three different textile plants belonging to the knit and wowen fabric finishing categories. They all process mainly cotton with a varying percentage of synthetic fabric and include in their processes all major finishing operations such as bleaching, dyeing, water proofing, application of special finishes, etc. The characteristic of the effluents evaluated in the experiments are outlined in Table 1. The values of the parameters listed in the Table exhibit striking differences which are presumably reflected in the achievable levels of biological treatability of each effluent.

TABLE 1 Characteristics of Textile Wastewater Evaluated in the Treatability Tests

Parameters	Plant No.1 (Woven fabric)	Plant No.2 (Knit fabric)	Plant No.3 (Knit fabric)
Total COD, C_{T0}	1240*	885	981
Soluble COD, S_{T0}	1176	800	535
Soluble BOD_5	680	422	170
TKN	144	23	40
Total P	2.2	16	14
pH	12.2	7.2	7.85

* all values in mgl^{-1} expect for pH

The experimental plan basically involved the determination of the COD components resistant to biodegration and the kinetic / stoichiometric constants associated with the degradable portion of the influent COD. The initial soluble inert fraction S_I and the soluble residual microbial products S_P were calculated for the effluents of plant No.1 and 2. The initial particulate inert COD was also assessed aside from the soluble residual components for plant No.3 as the particulate portion constitutes almost 45 % of the total COD of this particular wastewater. All analyses were performed in accordance with Standard Methods (1989). The soluble COD was defined as the filtrate through Whatman GF/C glass fiber filters, also used to quantify particulate components on a volatile suspended solids basis. Oxygen uptake rate measurements were conducted with a WTW OXİ DIGI 550 oxygenmeter and a recorder.

Determination of Soluble Residual COD

As previously mentioned, the assessment of the soluble residual components was performed by using the comparison method developed by Germirli *et al.*, (1991), observing 2 litre aerated batch reactors for a period long enough to reach a steady minimum soluble COD level. The reactors were initially seeded with 20 mg^{-1} of biomass acclimated to a 50 % wastewater + 50 % glucose mixture.

For plant No.1 effluent, the reactors were started with an initial wastewater COD of 1176 mgl^{-1} and a glucose COD of 1254 mgl^{-1}, and they were observed for 516 hours. The results illustrated in Fig.2 show that the minimum attainable soluble COD level for the plant effluent was 139 mgl^{-1}, whereas glucose exhibited a much lower level of 55 mgl^{-1}. Correcting the observed results to compensate for the difference between the initial biodegradable COD in the two reactors, S_I = 90 mgl^{-1} and S_P = 48 mgl^{-1} could be calculated to characterize the plant effluent. The corresponding stoichiometric coefficients were then computed as Y_I = 0.076 and Y_P = 0.044 .

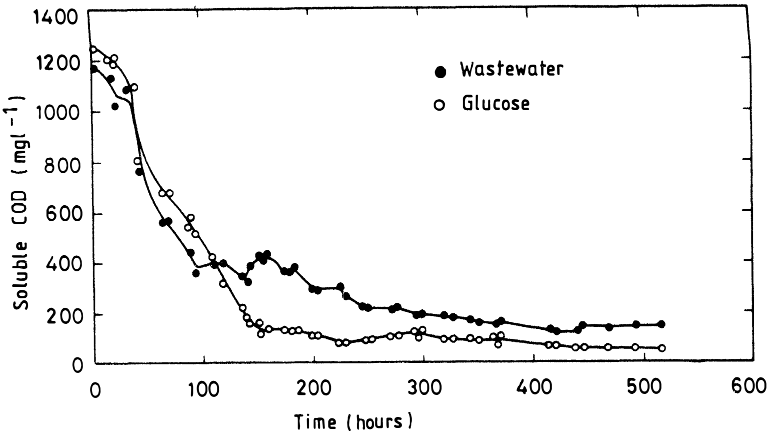


Fig. 2. Determination of residual soluble COD in the effluent of plant No.1.

The same experiment conducted for the effluent Plant No.2 and continued for 427 hours with an initial soluble COD concentration of 800 mgl^{-1} yielded minimum soluble COD concentrations of 120 mgl^{-1} and 40 mgl^{-1} for the wastewater and glucose reactors respectively. These values were found to correspond to S_I = 88 mgl^{-1} and S_P = 32 mgl^{-1} with $Y_I = 0.11$ and $Y_P = 0.04$.

The sample characterizing the plant effluent No.3 is quite different from the others as the initial BOD_5 / COD ratio is much lower as compared to the other textile samples tested. This property, probably due to extensive peroxide bleaching practiced in the plant,was also reflected in the level of soluble residual components: in the experiments, the initial soluble COD of 535 mgl^{-1} could only be lowered to 154 mgl^{-1} after 642 hours, corresponding to S_I and S_P fractions of 117 mgl^{-1} and 37 mgl^{-1} respectively. The calculated Y_I of 0.22 and Y_P of 0.088 are more than twice higher than the ones associated with the other effluents.

Determination of Particulate Residual COD

Inspection of the data presented in Table 1 indicates that the particulate COD was not significant for the first two plants whereas it constituted 45 % of the wastewater COD for Plant No.3. Consequently the proposed method was tested on this effluent to assess the particulate inert COD component. The results of the experiments conducted on three parallel batch reactors are given in Fig.3. It is noted that the reactor started with the total COD, C_{T0} stabilized around a final residual COD level of S_{R2} = 187 mgl^{-1}. Since S_{S0}, S_I and S_{P1} of the same wastewater were previously determined as 418 mgl^{-1}, 117 mgl^{-1} and 37 mgl^{-1} respectively, according to expression 17,

$$S_{P2} = 187 - 117 = 70\ mgl^{-1}$$

From equation 18 and 19:

$$C_{S0} = \frac{70}{37} 418 = 791\ mgl^{-1}$$

and

$$X_I = 981 - 791 - 117 = 73\ mgl^{-1}$$

This result indicates that only 16 % of the initial particulate COD is inert and yields the following COD composition for the wastewater of Plant No.3: C_{T0} = 981 mgl^{-1}; X_I = 73 mgl^{-1}; X_{S0} = 373 mgl^{-1}; S_I = 117 mgl^{-1}; S_{S0} = 418 mgl^{-1}.

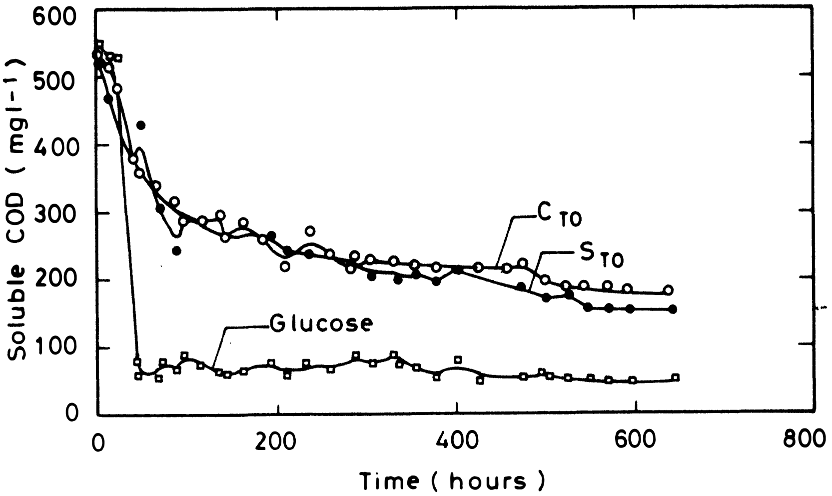


Fig. 3. Determination of residual particulate COD in the effluent of plant No.3

Determination of Kinetic and Stoichiometric Constants

Two sets of experiments were run on wastewater samples characterizing the effluents from Plants No.2 and 3. The first set of experiments were conducted for the assessment of $\hat{\mu}$, K_S and Y in 3-liter aerated batch reactors started with initial soluble COD concentrations of the effluents. The initial biomass inoculations were adjusted to maintain an S_{S0}/X_{A0} of around 20, a ratio that gives independent sensitivity functions for $\hat{\mu}$ and K_S (Dang *et al.*, 1989). The change in the total soluble COD, S_T with time was observed and evaluated by means of non-linear regression analysis using equations 1 to 5 modified for batch reactor behaviour. Fig.4 shows the experimental results together with the mathematical simulation for plant No.2.

The second set of experiments were devoted to the determination of the microbial decay coefficients; activated sludge samples were taken from the reactors used for the assessment of kinetic constants and placed in similar aerated batch reactors where oxygen uptake rate was followed over a period of 10 days (Marais and Ekama, 1976). The decay coefficient b was obtained as the slope of the plot of ln OUR versus time. The Task Group decay coefficient, b_H could then be calculated from the expression below:

$$b_H = \frac{b f_E}{f_P}$$

where

$$f_P = \frac{f_E(1 - Y - \alpha Y)}{(1 - f_E) + f_E(1 - Y - \alpha Y)}$$

f_E, the observed fraction of inert particulate products, is usually given a value of 0.20 in traditional models (Mc Kinney and Symons, 1962). The experimental information also enabled calculation of the rate coefficient α related to the generation of residual microbial products, S_P by means of expression 13. The results obtained for the two samples studied are summarized in Table 2.

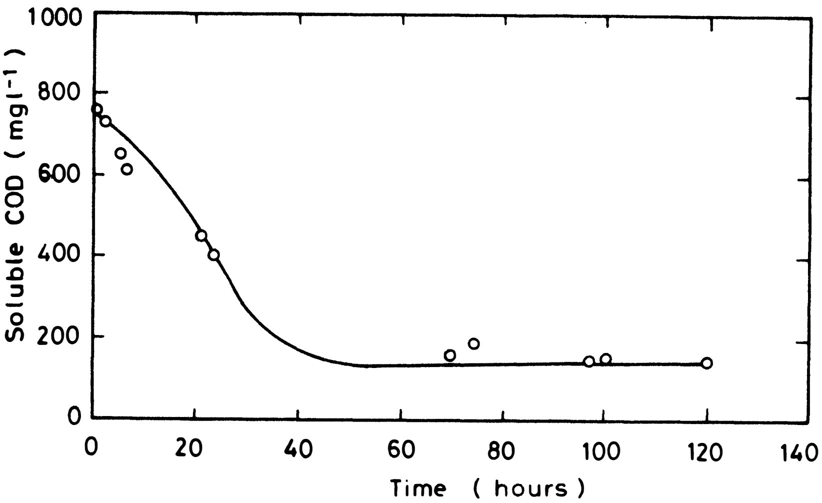


Fig. 4. Experimental results and model simulation for the determination of kinetic constants (plant No.2)

TABLE 2 Kinetic and Stoichiometric Constants Evaluated For Textile Wastewaters

Plant No.	Kinetic and Stoichiometric Constants					
	$\hat{\mu}$ (day^{-1})	K_S (mgl^{-1})	b_H (day^{-1})	Y mg cellCOD(COD)$^{-1}$	α	f_P
Plant No.2	2.0	60	0.5	0.6	0.03	0.087
Plant No.3	2.1	50	0.62	0.6	0.07	0.08

Biological Treatability Experiments

Parallel to the experimental studies elaborating the fundamental mechanisms responsible for the fate of COD components, a series of biological treatability experiments were carried out on wastewater samples from Plant No.1 and 2 using similar aerated batch reactors. The reactors were daily fed on a fill and draw basis to reach and maintain at least for five consecutive days a steady state condition and operation characterized by a preset organic loading rate. Consequently the observed experimental data could be interpreted to yield an empirical correlation between the effluent COD and the corresponding organic loading rate. The results are outlined in Table 3, together with the findings on residual COD components derived from the previously outlined experiments. The comparative evaluation of the two different experimental findings clearly shows that it is impossible to lower the effluent soluble COD below the threshold levels set by the respective soluble residual components.

TABLE 3. Results of Biological Treatability Experiments

Biological Treatability Results				Effluent Residual Components			
Organic Loading	Influent COD	Effluent COD		Influent COD	S_I	S_P	S_R
grCOD(grSS^{-1}d^{-1})	mgl^{-1}	Soluble COD mgl^{-1}	Total COD mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}	mgl^{-1}
Plant No.1				1176	90	48	138
0.20	1240	144	-				
0.30	1240	152	230				
0.40	1240	154	220				
Plant No.2				800	88	32	120
0.20	930	133	138				
0.27	930	129	177				
0.41	930	138	191				
0.41	1140	148	190				
0.52	1140	175	210				
0.87	680	178	336				
1.08	680	195	370				
1.15	875	252	413				
1.26	765	243	380				
1.43	875	266	509				

EVALUATION OF RESULTS AND CONCLUSIONS

The following points can be outlined to characterize the major observations and evaluations derived from this study.

1. For all the three textile plant effluents investigated in the study, the initial soluble inert COD was found to be a significant fraction of the organic content of wastewater; S_I concentrations varied between 88 - 117 mgl^{-1} with corresponding Y_I values in the range of 0.076 - 0.22. Similarly the Y_P coefficient, relating the formation of soluble inert microbial products to the degradable COD present in the wastewaters, was calculated to change between 0.04 and 0.09.

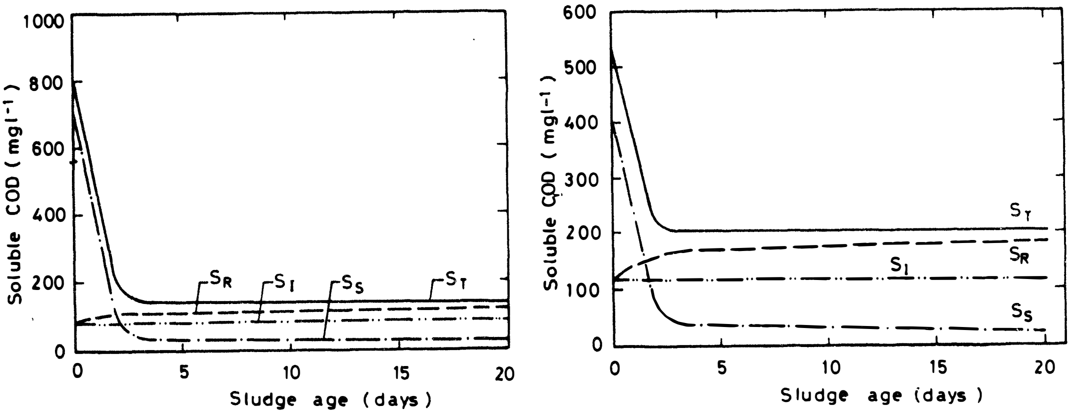
2. A method was defined for the experimental determination of the initial particulate COD and it was tested for the sample characterizing the Plant No.3 effluent. The results showed that 73 mgl^{-1}, corresponding to 16 % of the initial particulate COD, was not biodegradable.

3. The kinetic and stoichiometric coefficients evaluated for two of the textile effluents indicated that there were no differences of practical significance between the degradation rates of the biodegradable fractions of these wastewaters. Only $\hat{\mu}$ was found to be lower as compared to domestic wastewaters while the other parameters were in the same range.

4. An exellent agreement was observed between results of residual COD experiments and those of biological treatability studies, clearly showing that the effluent soluble COD could not be lowered by the simple expedient of reducing the organic loading rate beyond a threshold value which was essentially defined by the total residual COD.

5. By feeding the experimental findings related to the residual and degradable portions of COD in terms of appropriate rate coefficients as given in Table 2 into the set of continuity equations 1 to 5 describing the steady state operation of an activated sludge system with sludge recycle, it was possible to define a

relationship indicating the variation of the total soluble effluent COD with the sludge age. This simulation was performed for plants No.2 and 3 and shown in Fig. 5. They show that the effluent soluble COD would be almost entirely composed of residual components beyond a sludge age of 4 days. Consequently COD removal efficiency should not be expected to go higher than 86 % for Plant No.2 and 81 % for Plant No.3.



a) Plant No.2 b) Plant No.3

Fig. 5. Simulation of the effluent soluble COD

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