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The effect of mixing pharmaceutical and tannery wastewaters on the biodegradation characteristics of the effluents

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Abstract

This paper evaluated the effect of mixing the effluent of a pharmaceutical plant producing acetylsalicylic acid with tannery wastewater, on the biodegradation of the effluents. The evaluation involved the analysis of the oxygen uptake rate (OUR), profiles of each wastewater and the mixture by respirometry. Model calibration using the experimental OUR data identified major COD fractions and associated process kinetics for all samples analyzed. The tannery sample was a plain-settled effluent having a total COD of around 2200 mg/L with a readily biodegradable fraction of 15%. The same fraction was 57% in the pharmaceutical wastewater sample having a much stronger total COD content of 40,435 mg/L. Consequently, mixing of the pharmaceutical effluent with the tannery wastewater up to 38% of the total COD in the mixture increased the readily biodegradable COD fraction but had an inhibitory effect on the biodegradation kinetics. This effect was relatively lower on growth, but quite significant on the hydrolysis of the slowly biodegradable COD decreasing the maximum hydrolysis rate from 2.0 day^{-1} to 1.2 day^{-1}. Model evaluation of the respirometric data, as performed in this study sets a workable protocol for the assessment of the compatibility of different wastewater mixtures for biological treatability.

Keywords: Acetylsalicylic acid effluent; COD fractions; Process kinetics; Respirometry; Tannery effluent

1. Introduction

This study is mainly focused on investigating changes likely to occur in the biodegradation kinetics of a mixture of two wastewaters with different characteristics. A practical concern about receiving a pharmaceutical effluent into a full-scale activated sludge plant originally built and operated for the treatment of tannery wastewater initiated the study. The adopted experimental approach was essentially based on the scientific understanding of complex substrate biodegradation established in the last two decades. In fact, until recent past, overall substrate parameters, such as biochemical oxygen demand, have been the major obstacle in the accurate assessment of biodegradation. Promotion of the chemical oxygen demand (COD) has been an improvement as the utilized COD could establish an electron balance with biomass generated and dissolved oxygen consumed but the problem of defining the entire substrate concentration with a single parameter still persisted [1]. Identification of COD fractions with different biodegradation characteristics was the expected major achievement in this field [2], which triggered the development of respirometry for COD fractionation and biodegradation kinetics [3,4]. This also led the way to multi-component models that incorporated COD fractionation and promoted the oxygen uptake rate (OUR), as the major parameter for wastewater characterization and process kinetics [5]. This approach provided a new insight to the biodegradation characteristics of domestic sewage [6–8]. It was successfully applied to different industrial wastewaters [9–11].

Pharmaceutical industry often generates high-strength wastewaters, changing in character and quantity depending upon the products and related manufacturing processes. Generally, pharmaceutical effluents are compatible with conventional biological treatment [12,13]. Rosen et al. [14] reported that biological treatment of chemical synthesis based pharmaceutical wastewater provided high COD removal and toxicity. No specific information is so far available in the literature on COD

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Nomenclature

b_H	endogenous decay rate (day^{-1})
C_{T1}	total influent COD (mgCOD/L)
f_a	activity coefficient (mgCOD/mgCOD)
f_{ES}	soluble residual fraction (mgCOD/mgCOD)
f_{EX}	particulate inert fraction (mgCOD/mgCOD)
k_h	maximum specific hydrolysis rates (day^{-1})
K_S	half-saturation coefficient (mgCOD/L)
K_X	half-saturation coefficients for hydrolysis (mgCOD/mgCOD)
OUR	oxygen uptake rate (mg/L h)
S_H	rapidly hydrolysable COD (mgCOD/L)
S_I	soluble inert COD (mgCOD/L)
S_O	oxygen concentration (mgO_2/L)
S_P	soluble residual COD generated as metabolic products (mgCOD/L)
S_S	readily biodegradable COD (mgCOD/L)
S_{T1}	influent soluble COD (mgCOD/L)
X_H	active heterotrophic biomass (mgCOD/L)
X_I	particulate inert COD (mgCOD/L)
X_P	particulate inert metabolic products (mgCOD/L)
X_S	slowly hydrolysable COD (mgCOD/L)
Y_H	yield coefficient (mgCOD/mgCOD)

Greek symbols

μ_H	maximum specific growth rate (day^{-1})

fractionation and biodegradation characteristics of acetylsalicylic acid production effluent.

Leather tanning generates a strong and complex wastewater, due to a sequence of processes involving high water use and an inflow of different type of chemicals. Tannery effluent is one of the most extensively studied industrial wastewaters, in terms of its characteristics [15], effect of specific pollutants such as chromium on treatability [16] and specific pretreatment requirements [17]. Based on the information presented in the literature, a plain-settled tannery wastewater, as used in this study, is expected to have a total COD content of around 2000–2500 mg/L, mostly of particulate nature enmeshed with chromium and other suspended pollutants. Studies on tannery effluent also set a good example for respirometric evaluation wastewater characteristics. Orhon et al. [18] indicate that in the plain-settled tannery wastewater, only 79% of the total COD is biodegradable, with 19% readily biodegradable and the remaining 60% slowly biodegradable COD both in the soluble and particulate range. The biodegradation kinetics of tannery wastewaters has been evaluated in a wide range of studies and the enhancement of biological treatment of tannery effluents has been one of the major concerns in these studies [19–21]

The objective of the study was to evaluate the effect exerted on the biodegradation characteristics of the effluents under aerobic conditions when the effluent of a pharmaceutical plant producing acetylsalicylic acid is mixed into plain-settled tannery wastewater. The evaluation was performed by generating and analyzing the specific oxygen uptake rate profiles of each wastewater and the mixture by respirometry. Model calibration using experimental OUR data identified biodegradation fingerprints, including major COD fractions and associated process kinetics for all samples analyzed.

2. Materials and methods

2.1. The survey sites

The study was conducted in the *Istanbul Organized Leather Tanning Industrial District*, located in Tuzla, Istanbul. The district presently houses around 110 tanneries processing both cattle hide and ship skin, resulting in an average total wastewater flow of around 12,000 m^3/day. In the district the entire combined wastewater is pretreated by plain settling prior to biological treatment by activated sludge. Recently, the district has served to a number of scientific studies focused on microbial ecology and system optimization for both organic carbon and nitrogen removal [22–24]. The study first involved a survey of 5 months on conventional characterization of the plain settling effluent fed to the activated sludge system. The results obtained, as outlined in Table 1, indicated that the biological treatment influent could be characterized by an average COD of 2170 mg/L with a soluble (filtered) fraction of 1070 mg/L, a total suspended solids (TSS), of 735 mg/L, a total sulfide of 70 mg/L and a total chromium of 35 mg/L, much the same as reported in earlier similar studies.

The pharmaceutical plant investigated in the study is an acetylsalicylic acid production facility, located near the *Istanbul Organized Leather Tanning Industrial District*. The production capacity is around 4500 kg/day in a batch wise operation during 6 days a week and 300 days a year. The wastewater flow generated from acetylsalicylic acid production is around 20–25 m^3/week with an average daily flow of 2.5 m^3. A similar survey on wastewater characteristics conducted on the plant for 3 months indicated that the process wastewater was quite strong with an average COD concentration of 40,300 mg/L, highly fluctuating in the range of 8000–76,000 mg/L. The wastewater

Table 1
Conventional characterization of the biological treatment influent at *Tuzla Organized Leather Tanning Industrial District*

Parameter	Unit	Value	Average
pH	–	6.9–8.7	7.4
TSS	mg/L	430–1080	735
Total COD	mg/L	1165–3000	2170
Filtered COD	mg/L	560–1915	1070
BOD_5	mg/L	500–1600	1110
TKN	mg/L	170–330	245
Filtered TKN	mg/L	112–282	195
NH_4–N	mg/L	73–210	130
S^{-2}	mg/L	10–145	70
Total Cr	mg/L	15–65	35
SO_4^{-2}	mg/L	1145–2345	1700
Cl^-	mg/L	4100–7130	5910
Alkalinity	mg/L	510–2200	1220
Oil & grease	mg/L	110–1475	355
Flowrate	m^3/day	2948–17,838	12,175

characterization studies of the acetylsalicylic acid production effluents revealed that, the wastewater essentially includes organic chemicals, but its fraction in the mixture is small enough not to affect the other characteristics of tannery effluent.

The study was primarily undertaken to set the scientific basis for either providing a separate full treatment for the pharmaceutical effluent, or mixing the pharmaceutical effluent with the tannery wastewater for joint treatment at the existing plant of the *Leather Tanning Industrial District.* The decision depended upon the outcome of the study on the magnitude of the adverse effect of the pharmaceutical effluent, if any, on the biodegradation characteristics of the mixture.

2.2. Experimental design

As mentioned before practical implications are important in the scientific interpretation of the results. Accordingly, the ratios of the wastewater mixture were adjusted, with a safety margin, taking into account the respective flow rate and organic loads of the two wastewaters. Currently, the average tannery wastewater flow rate discharged into the existing treatment system is around 80,000 m^3/week, corresponding to a COD load of 174,000 kg/week. On the other hand, wastewater generated by the pharmaceutical plant is around 20 m^3/week, with a COD load of 800 kg/week, amounting to only 0.46% of the COD load in the tannery wastewater. In the weekends when the flow rate of the tannery effluent drops down to 3000 m^3/day, the ratio of the COD loads increases to 1.6%. It should be noted that the calculated values are only meaningful when the pharmaceutical effluent is continuously discharged and mixed with the tannery wastewater. Considering that the pharmaceutical effluent is generated batch wise, it is likely to be mixed with the tannery wastewater as a pulse, creating short-term, much higher levels. Therefore the study was expanded for scientific purposes, to also explore the mixing levels where inhibitory effects could be observed and/or increased. Accordingly, dilutions were adjusted around the actual mixing range (1–2%) and also at much higher levels (16–38%) to be able to interpret the OUR results at different scales

2.3. The respirometric procedure

The biomass sampled from the *Tuzla Tannery Organized Industrial District* wastewater treatment plant was used in biological treatability experiments. The 4-L fill-and-draw reactor, equipped with diffused aeration devices was operated at steady state with a sludge age of 10 days and a hydraulic retention time (HRT) of one day for a period of 2 months.

The respirometric procedure for the assessment of major kinetic and stoichiometric coefficients such as the readily biodegradable COD, S_S, the maximum heterotrophic growth rate, μ_H, and the heterotrophic yield coefficient, Y_H, involved using 1 L batch reactors. In the OUR test was conducted with an inhibitor (Formula 2533^{TM}, Hach Company, Loveland, Colorado) for the prevention of any possible interference induced by simultaneous nitrification. The reactor was initially fed with the wastewater sample, seeded with appropriate biomass to start with a suitable initial substrate/biomass (C_{T1}/X_{T1}) ratio and constantly aerated to maintain a dissolved oxygen concentration of 6–8 mg/L. The readily biodegradable COD, S_{S1} was determined in accordance with the method suggested by Ekama et al. [3]. The assessment of the readily biodegradable substrate concentration relies on the observation that the OUR may be experimentally managed to stay approximately constant during the consumption of S_S and drops to a second lower level when S_S is depleted. Therefore, S_S may be calculated from the equivalent oxygen consumption which is equal to the area between the OUR curve defined by the two plateaus, in accordance with $S_S = \Delta O_2/(1 - Y_H)$ expression [3]. For the assessment of heterotrophic yield, Y_H by using the experimental method given by Cokgor [25], soluble COD analysis were also performed on samples taken for OUR measurements, yielding soluble COD profiles together with OUR profiles during the experiments. For the assessment of the maximum heterotrophic growth rate by means of respirometric test, the reactors were run at a C_{T1}/X_{T1} ratio of 4–5 gCOD/gVSS as recommended by Kappeler and Gujer [26]. OUR measurements were conducted with a WTW OXI DIGI oxygen meter. Hydrolysis rate coefficients, k_h and K_X, and half-saturation coefficient, K_S were determined by applying curve fitting techniques to the OUR profile obtained for S_{S1} determination. The modeling studies were performed using the simulation program Aquasim [27].

Particulate and soluble inert COD for the tannery wastewater was determined with the aid of methods proposed by Orhon et al. [28] and Orhon et al. [29]. The inert COD test involved three aerated batch reactors, of 3 L volumetric capacity each, one fed with the unfiltered wastewater, C_{T1}, and second with the filtered wastewater, S_{T1} and, the third the glucose wastewater, S_{G1}. The microbial seed obtained from a lab-scale fill and draw aerobic reactor operated under steady state with the same wastewater, was added to secure an initial biomass concentration of around 40 mg/L VSS in the reactors. Aliquots removed periodically from the mixed liquor were analysed for total and soluble (filtered) COD. The measurements were continued until the observation of final threshold values of the total and soluble COD at the depletion of all biological activity.

2.4. Biodegradability tests

The biodegradability tests were conducted using two 4 L fill and draw reactors, one fed with tannery effluent as the control reactor and the second fed with tannery effluent and pharmaceutical effluent mixture. The continuously aerated fill and draw reactors were operated with manual feeding and manual sludge and effluent withdrawal. The organic loading rate of the 4 L reactors were maintained as 0.2 gCOD/gMLSS day, where the biomass concentrations were 3000 mg TSS/L under steady state conditions. Since the necessary stoichiometric amount of nitrogen for microbial growth was present in tannery wastewaters nutrient solutions of phosphate ions were added in order to maintain the elementary need for phosphorus and to provide the required buffer capacity to the activated sludge system. The reactors were operated with hydraulic retention times of 1 day and the sludge retention times were maintained as 10 days. The maximum sludge volume index (SVI) was determined as 120 mL/g, during the experimental study.

2.5. Analyses

All analyses in terms of conventional parameters were performed as defined in Standard Methods [30]. The soluble (filtered) COD was defined as the filtrate through Whatman GF/C glass fiber filter that were also used to assess TSS and VSS parameters.

3. Experimental results

3.1. Respirometric studies

A sequence of six OUR tests were conducted, the first one (Run 1), on the tannery wastewater, the second one (Run 2), on the pharmaceutical effluent and the other four runs (Runs 3.1–3.4) on different mixtures of the two wastewaters where the COD of the pharmaceutical effluent represented 1, 2, 16 and 38% of the total COD of the mixture. The pharmaceutical effluent was diluted to an initial COD of 688 mg/L in order to obtain optimum results [31]. Appropriate identification of kinetic coefficients necessitates optimal experimental design and this is particularly true for hydrolysis kinetics. In this context the appropriate organic strength of the feed in respirometric tests in the study was evaluated and the wastewater was diluted a level of around 700 mg/L COD to obtain good interpretation of the resulting OUR curve.

Preliminary OUR tests were performed at high initial substrate/biomass ratios as defined by Kappeler and Gujer [26] for the determination of the maximum heterotrophic growth rate, μ_H. As shown by Fig. 1, the μ_H value for the tannery wastewater was found as 2.54 day^{-1}. This level, although consistent with the mean value of 2.2 day^{-1}, previously determined for the same plain-settled wastewater by Orhon et al. [18] is significantly lower than the range of 4.8–6.5 day^{-1} ascertained for domestic sewage [32], indicating that tannery wastewater after plain settling is still subject to significant inhibitory action, probably because of the presence of trivalent chromium and sulfide enmeshed with biomass and other unidentified inhibitors. A similarly low μ_H value of 2.5 day^{-1} was also determined for the pharmaceutical effluent, presumably due to substrate inhibition.

The heterotrophic specific growth rate values determined by the method of Kappeler and Gujer [26] were used only as a preliminary estimation. Like all other parameters experimentally assessed by means of direct procedures, they were verified by the calibration of the model using the experimentally obtained the OUR profiles. The respirometric tests conducted for tannery wastewater, pharmaceutical effluent and the mixtures were used for the assessment of the COD fractions and modeling studies. The OUR curves obtained for tannery and pharmaceutical wastewaters were used to estimate the biodegradable COD fractions using the amount of oxygen utilized during the test. The readily biodegradable COD fraction, S_S was estimated according to the method described by Cokgor [25] with a heterotrophic yield coefficient, Y_H, of 0.67 mg cellCOD/mgCOD for tannery wastewater [18] and 0.55 mg cellCOD/mgCOD for pharmaceutical wastewater. It should be noted that the OUR studies on the mixture were designed to underline the inhibitory effect of the pharmaceutical wastewater. The organic feed was primarily from the tannery wastewater and therefore biomass was acclimated to tannery wastewater for its metabolic functions, which were impaired at certain level by the addition of the other waste stream. Thus, the Y_H value of 0.67 mg cellCOD/mgCOD, associated with the tannery wastewater was adopted for the experimental evaluation of the mixtures. The endogenous decay rate, b_H was accepted as 0.15 day^{-1} [18,33]. The stoichiometric values for the microbial products generated by decaying biomass, f_{ES} and f_{EX} were accepted as 0.1 and 0.2 respectively. The selected values for f_{ES} and f_{EX} were verified and all the other kinetic coefficients were determined by model calibration of the experimental OUR data. The multi-component model adopted for respirometric evaluation basically has, as shown in the commonly accepted matrix format in Table 2, the organic carbon removal part of ASM1 [5]. It was modified for endogenous respiration as conveniently utilized in many similar modeling studies for industrial wastewaters [10,11].

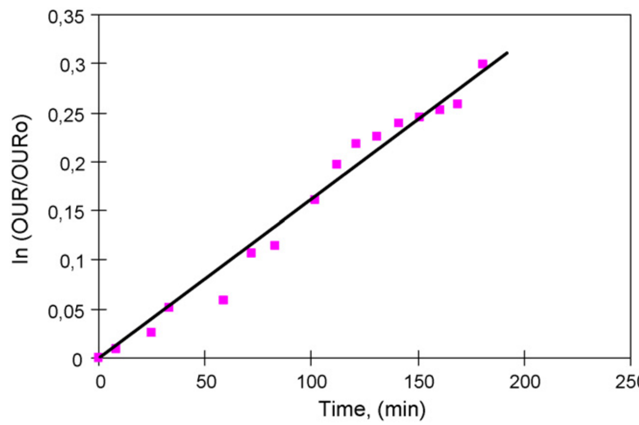

Fig. 1. Respirometric determination of the maximum heterotrophic rate for biomass fed with tannery wastewater.

Table 2
Matrix representation of the model used for respirometric evaluation

Component→	1	2	3	4	5	6	Process rate
Process↓	S_S	X_S	X_H	X_P	S_P	S_O	$ML^{-3}\,T^{-1}$
Growth	$-\frac{1}{Y_H}$		1			$-\frac{(1-Y_H)}{Y_H}$	$\mu_H \frac{S_s}{(K_s+S_s)} X_H$
Hydrolysis	1	−1					$k_h \frac{X_s/X_H}{(K_X+X_S/X_H)} X_H$
Decay			−1	f_{EX}	f_{ES}	$-(1-f_{EX}-f_{ES})$	$b_H X_H$
Parameter (ML^{-3})	COD	COD	cellCOD	COD	COD	O_2	

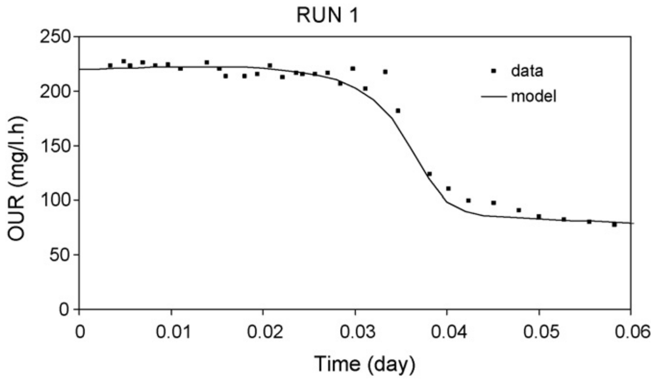

Fig. 2. Model simulation of the experimental OUR profile for the tannery wastewater.

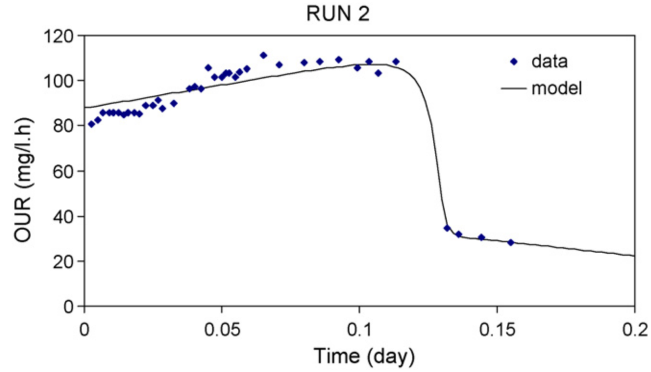

Fig. 3. Model simulation of the experimental OUR profile for the pharmaceutical wastewater.

Evaluation of the OUR profile illustrated in Fig. 2 yielded a total inert COD fraction, C_{I1}, of 493 mg/L for tannery wastewater, indicating that only 77% of the total COD was of biodegradable nature. Inert organics, depending on their nature and characteristics may sometimes lead to inhibitory effects and bad treatment performance. Recently studies were conducted to reduce inert COD by ozonation [23,34]. The level of the readily biodegradable COD, S_{S1} was only 324 mg/L, around 15% of the total COD and 19% of the biodegradable COD, where the bulk of 1367 mg/L could be defined as slowly biodegradable COD, X_{S1}. The selected model calibrates well, as shown in Fig. 2, the experimental OUR data, verifying the previously computed stoichiometric and kinetic coefficients yielding a value of 2.0 day^{-1} for the hydrolysis rate coefficient, k_h and 0.1 mgCOD/mgCOD for the hydrolysis saturation coefficient, K_X. As expected, these values are lower than the corresponding levels associated with domestic sewage [8].

Fig. 3, illustrating calibration of the OUR profile with the same model, reflects the different character of the pharmaceutical wastewater, quite compatible with biodegradation, where the readily biodegradable COD accounts for 57% of the total COD content, with a lower slowly biodegradable COD and the total inert COD of around 10%, almost entirely of particulate nature. Model calibration provides a similar verification for the calculated coefficients and indicates a slightly better hydrolysis with a k_h value of 2.2 day^{-1} and a K_X value of 0.05 mgCOD/mgCOD. Comparative evaluation of the biodegradation characteristics of the two wastewaters does not seem to warrant a major adverse effect, an assumption that needs to be verified by the respirometric analysis of the mixture.

Model evaluation of the experimental runs 3.1–3.4 related to wastewater mixtures, where the relative contribution of the pharmaceutical wastewater varied in the range of 1–38% of the total COD of the mixture, is outlined in Table 3. The parameter estimation results obtained by using the secant method provided by Aquasim, were only used for the first estimation of the coefficient pairs and the final values have been determined by the comparative evaluation of the simulation results of all the experimental runs. The displayed data indicates a noticeable impact of the pharmaceutical effluent both on growth and hydrolysis: the maximum heterotrophic growth rate was reduced from 2.54 day^{-1} to 2.35 day^{-1} in Run 3 (16% COD) and to 2.20 day^{-1} in Run 6 (38%COD), a total decrease of around 13%, together with an increase in the half-saturation coefficient for growth, K_S, from 5 mg/L to 50 mg/L, also indicating a competitive type of an inhibitory adverse effect. The impact was more pronounced on the hydrolysis of the slowly biodegradable COD, where a decrease was induced on the hydrolysis rate coefficient, reaching 40% for Run 6 (38%COD), with a slight similar increase in the half-saturation coefficient for hydrolysis, K_X. As evaluated from the interpretation of the OUR profiles (Figs. 4 and 5), the negative effect was slight, although gradually increasing in runs 3.1, 3.2 and 3.3, but exhibited a significant increase in the final run (Run 3.4) where the pharmaceutical effluent addition corresponded to 38% of the total COD in the mixture. Based on experimental evaluation, this level should be interpreted as the threshold level for significant inhibitory impact. The corresponding OUR profile given in Fig. 5b provides a clear indication of this negative impact.

Table 3
Kinetic characteristics of biomass fed with wastewater mixtures assessed by model calibration using the OUR profiles

Wastewater	Fraction of pharmaceutical effluent added (% total COD)	Y_H (gCOD/gCOD)	$\hat{\mu}_H$ (day^{-1})	K_S (mg/L)	k_h (day^{-1})	K_X
Run 1 (tannery effluent)	–	0.67	2.54	5	2.0	0.1
Run 2 (pharmaceutical effluent)	100	0.55	2.50	9	2.2	0.05
Run 3.1 (mixture)	1	0.67	2.45	10	1.9	0.15
Run 3.2 (mixture)	2	0.67	2.40	12	1.8	0.15
Run 3.3 (mixture)	16	0.67	2.35	12	1.8	0.15
Run 3.4 (mixture)	38	0.67	2.20	50	1.2	0.15

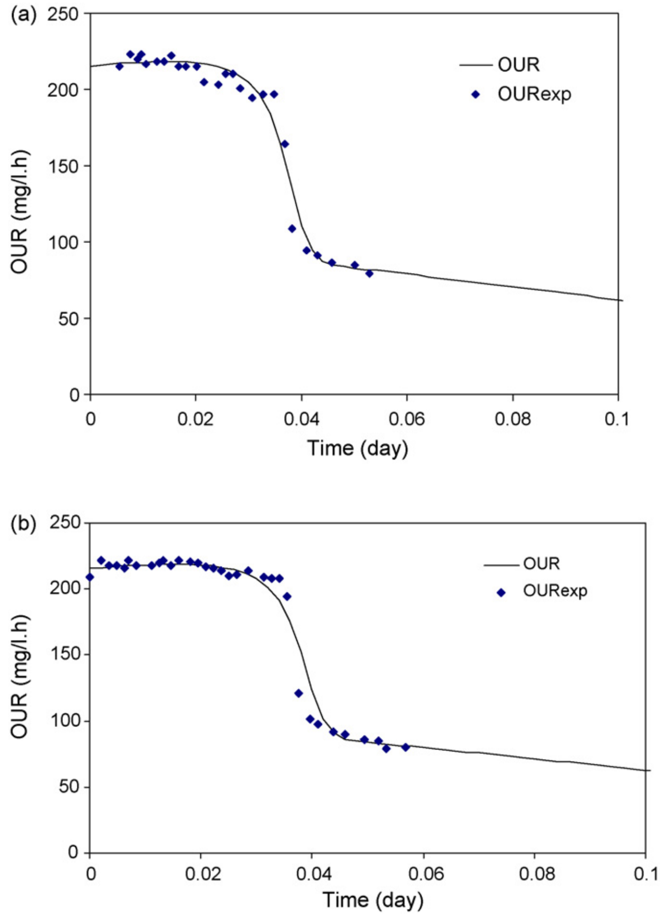

Fig. 4. The OUR profiles obtained in: (a) Run 3.1, with 1% COD contribution of the pharmaceutical effluent and (b) Run 3.2, with 2% COD contribution of the pharmaceutical effluent.

3.2. Biodegradability studies

A laboratory-scale biodegradability study was carried out to verify the respirometric results. For this purpose two fill and draw reactors of 4 L volume were operated at steady state at an organic loading rate of 0.2 gCOD/gMLSS day, approximating the actual operation of the activated sludge system treating tannery wastewater. The reactors were seeded and started up with biomass taken from the activated sludge plant used for the treatment of tannery wastewater. One of the reactors was set as a control unit and fed with the tannery effluent alone. The other was also started with the tannery wastewater at the beginning and then operated with successive additions of the pharmaceutical effluent increasing in the range of 0.6–11% on the total COD basis, this way covering with a safety margin the actual operation likely to occur based on existing data on wastewater generation. The upper level of the mixture was maintained well below the threshold value of 38% observed to induce inhibitory effects. The test was conducted mainly to observe the COD level in the treated effluent and to assess the possible impact of pharmaceutical addition on the COD removal efficiency of the activated sludge. Fig. 6, including the results from both reactors, show that the effluent soluble COD range of 200–250 mg/L obtained with the tannery wastewater

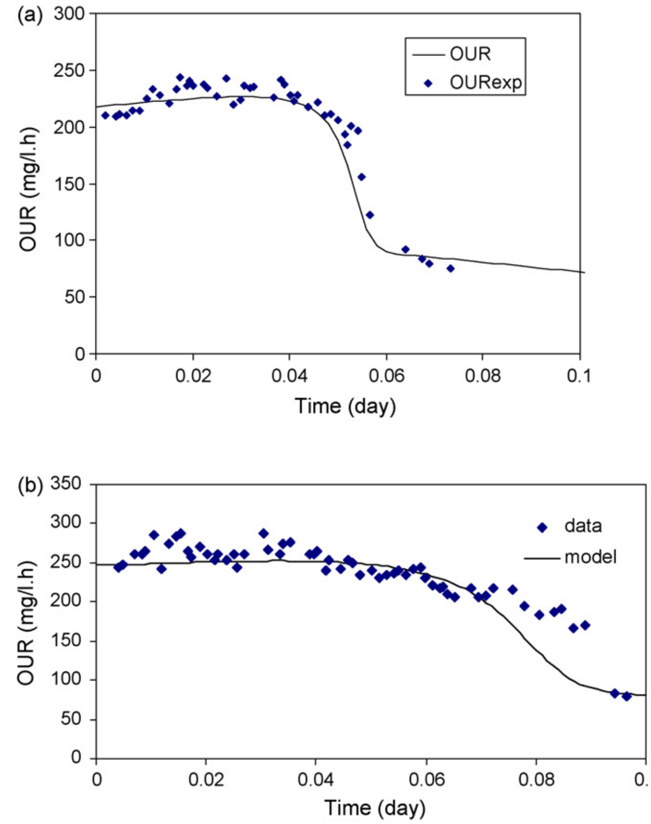

Fig. 5. The OUR profiles obtained in: (a) Run 3.3, with 16% COD contribution of the pharmaceutical effluent and (b) Run 3.4, with 38% COD contribution of the pharmaceutical effluent.

alone was not impaired by the addition of the pharmaceutical effluent in the tested range. This range essentially represents the soluble inert COD initially present in the tannery wastewater and soluble inert microbial products, since the inert COD content of the pharmaceutical effluent is mainly particulate and the soluble residual COD of the pharmaceutical effluent is negligible.

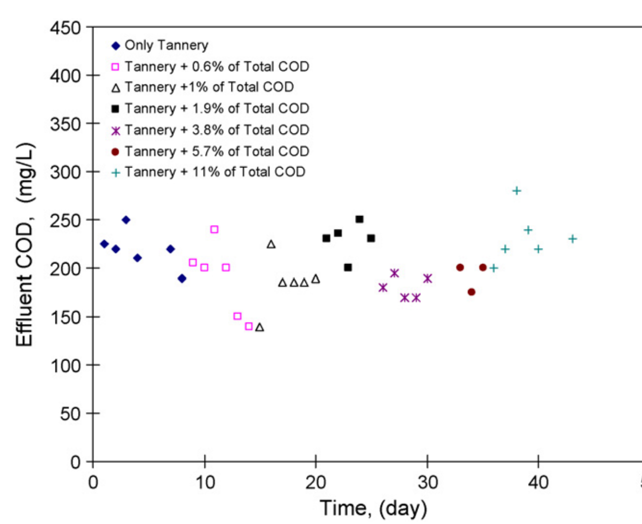

Fig. 6. The effluent COD of the reactor operated with tannery wastewater and different amounts of pharmaceutical wastewater mixtures.

4. Conclusions

In the light of the results and evaluations presented above, the conclusive remarks of this study may be outlined as follows:

In this study, evaluation of the experimental OUR data by means of a multi-component model with a mechanistic structure compatible with the experiments yielded consistent and reliable information on biodegradation kinetics for a sequence of experiments with different mixtures of pharmaceutical and tannery wastewaters. Interpretation of the kinetic data indicated an adverse effect on microbial growth with a competitive type of inhibitory action, which resulted in a 10-fold increase in the value of the half-saturation coefficient, K_S from 5 mg/L to 50 mg/L. It also showed a more pronounced inhibitory impact on the hydrolysis of the slowly biodegradable COD, reducing the hydrolysis rate by 40%. The threshold level of the significant impact could be defined for a mixture where the addition of the pharmaceutical effluent accounted for 38% of the total COD.

Model evaluation and calibration of the experimental OUR data also served as a useful fingerprint for each wastewater, assessing COD fractionation and specific biodegradation kinetics. Low growth and hydrolysis kinetics associated with tannery wastewater on the basis of the OUR results reflect the combined effect of all the specific pollutants, such as trivalent chromium, sulfide, etc., inherently present in this type of wastewater. While this evaluation indicated a higher readily biodegradable COD content of around 57% and slightly higher process kinetics for pharmaceutical effluent as compared to tannery wastewater, it also identified its significant inhibitory characteristics in the mixture. This way, it underlined the danger of extrapolating the results and drawing misleading conclusions for the kinetic behavior of the mixture, which was totally different than what was indicated by the analysis of the wastewaters on an individual basis.

The experimental results could also be interpreted from a practical aspect that mixing of the pharmaceutical effluent to tannery wastewater for joint treatment, considering the actual flow rates and organic loads of the two wastewaters, would stay well below the threshold level defined by the experimental results of this study and therefore would not pose a noticeable problem for the efficiency of treatment.

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