Experimental evaluation of the nitrification kinetics for tannery wastewaters

Derin Orhon*, Esra Ates Genceli and Seval Sözen

Istanbul Technical University, Environmental Engineering Department, I.T.Ü. İnsaat Fakültesi, Ayazaga Kampüsü, 80626 Maslak, Istanbul, Turkey

Abstract

The paper outlines results of the experimental assessment of nitrification kinetics applicable to tannery wastewaters and the inhibitory effects of selected pollutants on nitrification. The average net growth rate of nitrifiers was measured as 0.32 d^{-1} at 20°C and 0.10 d^{-1} at 10°C for tannery wastewaters subjected to plain settling. This kinetic coefficient was observed to increase to 0.43 d^{-1} at 20°C with chemical settling. Parallel experiments with synthetic waste containing only NH_4Cl revealed the strong inhibitory character of tannery wastewater. Chromium was observed to be partly responsible for the inhibitory effect which was mainly induced by chloride, inherently present in this type of wastewaters.

Introduction

Growing concern over improvement of receiving water quality imposes stringent restrictions on wastewater discharges. In this context, nitrogen is now rigidly controlled, especially in sensitive coastal areas (Orhon et al.,1999a). This approach necessitates review and re-evaluation of existing conventional treatment schemes for significant nitrogen sources.

Tannery effluents exhibit all the characteristics of a strong wastewater, mainly with respect to their organic carbon and nitrogen content. In a recent study conducted on wastewaters from an organised industrial district housing a large number of tanneries, the concentrations of conventional polluting parameters such as COD and TKN were assessed as 5 000 mg·ℓ^{-1} and 350 mg·ℓ^{-1} respectively, yielding a COD/N ratio of around 14 (Ates et al., 1997); as outlined in Table 1, plain settling was observed to lower the COD concentration to 2 200 mg·ℓ^{-1}; the corresponding TKN level obtained was 225 mg·ℓ^{-1}, corresponding to a reduction of only 37%. In the same study, chemical treatment provided a slight improvement in TKN removal as outlined in Table 2. The limitations of the physico-chemical treatment could be explained by the fact that TKN in tannery wastewaters involved a significant NH_3-N fraction remaining intact, if not slightly increased due to ammonification during settling. Consequently, aerobic biological treatment is prescribed for simultaneous carbon and nitrogen removal from tannery wastewaters (Macchi et al., 1991; Szpyrkowicz et al., 1991).

The limiting step for N removal is nitrification, a process which is sensitive to inhibitory effects and which requires long aerobic sludge ages. The latter is also a requirement for the breakdown of the slowly biodegradable matter constituting the major COD fraction in tannery wastewaters (Orhon et al., 1999b; c). In a study conducted with sequencing batch reactors, a sludge age of 20 d was found to secure maximum nitrogen removal (Yamamoto and Win, 1991). Similarly, a continuous-flow activated sludge system fed with raw tannery effluents with a COD/N ratio of 6 to 8 and operated at an F/M range of 0.25 to 0.34 kgCOD(kgVSS·d)$^{-1}$ was reported to achieve 94% COD and 97% NH_3-N removal (Szpyrkowicz et al., 1991).

Table 1
Characterisation of Raw Wastewaters

Parameters mg·ℓ^{-1}	Raw wastewater	Homogenisation outlet	Primary clarifier effluent
Total COD	5 094	4 506	2 216
Soluble COD	2 336	1 345	1 187
BOD_5	1 760	1 402	958
SS	2 229	2 988	794
VSS	-	-	506
TKN	358	367	226
Org N	223	209	62
NH_3-N	135	158	164
Total P	-	-	5.1
Total Cr(Cr^{+3})	116	132	41
Sulphur ($S^{=}$)	51	47	27

This study was designed to evaluate nitrification in tannery wastewaters in a way that is meaningful from the standpoint of both the mechanism of related microbial kinetics and practical problems generated by inhibitory effects. In this context, it basically involved the experimental assessment of the maximum specific growth rate for autotrophic biomass, $\hat{\mu}_A$. In parallel experiments, this parameter was also measured on synthetic waste and on samples specifically prepared to include different levels of chromium and salinity, for the evaluation of the inhibitory character of tannery wastewaters.

Experimental

The experiments were performed on settled wastewater samples, using the effluent from the plain sedimentation unit of the treatment plant serving the Istanbul Organised Leather Tanning Industrial District located in Tuzla/Istanbul. The organised district, planned for a capacity equivalent to a wastewater flow rate of 36 000 $m^3 \cdot d^{-1}$, presently houses around 110 tanneries processing both cattle hide and sheepskin and generating a wastewater flow in

* To whom all correspondence should be addressed.
☎90 212 285 3410; fax 90 212 285 6587; e-mail: dean@srv.ins.itu.edu.tr
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TABLE 2
RELATIONSHIPS BETWEEN MAJOR PARAMETERS

Parameters mg·ℓ⁻¹	District I (Tuzla)		District II (Çorlu)		District III (Biga)	
	Initial[1]	Treated	Initial[2]	Treated	Initial[3]	Treated
Total COD	5 756	1 050	4 705	1 108	4 180	1 120
Soluble COD	1 170	-	1 600	-	1 495	-
SS	2 640	248	2 300	128	2 070	205
TKN	363	208	-	-	250	175
Total Cr (Cr^{+3})	42	<0.5	167	1.9	65	0.35
Sulphur ($S^{=}$)	78	24	42	10.6	68	16

[1] Homogenisation outlet; lab-scale primary effluent
[2] Homogenisation outlet; full-scale
[3] Raw wastewater; lab-scale

the range of 10 000 to 12 000 m^3d^{-1}. The activated sludge used in the acclimation stage of the laboratory experiments was also provided from the aeration tank of the same treatment unit, operated for both organic carbon and nitrogen removal.

The experiments for the measurement of the specific growth rate for nitrifiers were conducted in 1 ℓ aerated batch reactors seeded with nitrifying acclimated sludge sustained at steady state in a 3 ℓ fill-and-draw reactor operated at a sludge age of 20 d. The kinetic analysis on each sample representing different inhibitory conditions was carried out using a set of three parallel batch reactors operated under the same conditions and the corresponding result was expressed as the average value of the individual evaluations of the experimental data obtained from each reactor. Air supply to the reactors was adjusted to maintain a dissolved oxygen (DO) concentration of above 2 $mg \cdot \ell^{-1}$. Experiments were conducted mainly at 20 and 10°C, in a pH range of 7.5 to 8.5 and with no alkalinity limitations. 1 N $NaHCO_3$ and 1 N HCl solutions were used for alkalinity and pH adjustments, where needed. CO_2 was bubbled through the reactors for pH control. The experimental evaluation involved the observation of the increase in the N_{OX}-N profile with time, due to nitrification. The observation was continued for 7 to 10 d, depending on the NH_3-N strength of the wastewater tested. It should be noted that the extent of nitrification in a batch reactor is directly related to the amount of NH_3-N oxidised in the process. However, the use of NH_3-N for evaluating the value of $\hat{\mu}_A - b_A$ in activated sludge is limited, since ammonia nitrogen also serves as the basic nitrogen source and incorporated into biomass at the same time as it is oxidised. Consequently, the concentration of the oxidised nitrogen, N_{OX}-N, is a much more convenient parameter for this purpose, mainly because N_{OX}-N is the only model component solely related to autotrophic growth. Therefore N_{OX}-N should reflect the total oxidised nitrogen concentration and it has to be measured as NO_2^--N+ NO_3-N, since it is conceptually defined and used as an indirect parameter equivalent to the level of NH_3-N oxidised in the nitrification process.

In all experiments testing inhibitory effects, the assessment of the maximum specific growth rate for nitrifiers was also measured for a synthetic waste solution inoculated with biomass previously acclimated to tannery wastewaters. The synthetic waste was prepared as described by O'Conner (1972), to sustain nitrification only; it contained 10 $m\ell \cdot \ell^{-1}$ of the basic buffer and minerals solution

TABLE 3
BUFFER AND MINERAL SOLUTIONS FOR THE SYNTHETIC WASTE

Solution A	K_2HPO_4	320g·ℓ⁻¹
	KH_2PO_4	160g·ℓ⁻¹
	NH_4Cl	120g·ℓ⁻¹
Solution B	$MgSO_4\ 7\ H_2O$	15 g·ℓ⁻¹
	$FeSO_4\ 7\ H_2O$	0.5 g·ℓ⁻¹
	$ZnSO_4\ 7\ H_2O$	0.5 g·ℓ⁻¹
	$MnSO_4\ 3\ H_2O$	0.5 g·ℓ⁻¹
	$CaCl_2$	2.0 g·ℓ⁻¹

defined in Table 3, with no organic carbon source. The nitrogen content of the synthetic waste was roughly maintained at 200 $mgN \cdot \ell^{-1}$, a level compatible with plain-settled tannery wastewaters, by adding an appropriate amount of NH_4Cl. A similar alkalinity adjustment was made by means of a 1 N $NaHCO_3$ solution.

Chromium was supplied using the precipitate of a $KCr(SO_4)_2.12H_2O$ solution obtained by means of 5% lime addition, adjusting the pH to 8.5. Free trivalent chromium additions were made from the liquid phase of the same $KCr(SO_4)_2.12H_2O$ solution by appropriate pH adjustments in the activated sludge reactors.

All analyses were performed in accordance with *Standard Methods* (1989). The soluble (filtered) COD was defined as the filtrate through Whatman GF/C glass fiber filters with an effective pore size of around 1 µm. Oxidised nitrogen (N_{OX}-N) measurements were conducted by means of a Chem Lab autoanalyser, using the hydrazine reduction method.

Conceptual basis for evaluation

The experimental evaluation relies on the assessment of the maximum specific growth rate for autotrophic biomass, $\hat{\mu}_A$, for tannery wastewaters under different conditions. This kinetic coefficient is the most critical parameter for the nutrient-removing single-sludge activated sludge process, as it defines maintenance conditions of

the slowly growing nitrifiers within the mixed activated sludge population and consequently, the design value for the sludge age of the system. For the experimental calculation of this parameter, a laboratory-scale batch reactor is preferred, as it enables a simpler interpretation of the reaction kinetics involved. Nitrification kinetics involve at least the following three model components: ammonia nitrogen, DO and oxidised nitrogen. The utilisation of the first two is often complicated by the fact that they also interfere with heterotrophic growth. The generation of oxidised nitrogen, however, is solely related to nitrification and the fate of oxidised nitrogen concentration, S_{NO} may conveniently be monitored on the basis of the following mass balance equation:

$$S_{NO} = S_{NO0} + \frac{\hat{\mu}_A \; X_{A0}}{Y_A(\hat{\mu}_A - b_A)} \; e^{(\hat{\mu}_A - b_A)t} - \frac{\hat{\mu}_A \; X_{A0}}{Y_A(\hat{\mu}_A - b_A)} \quad (1)$$

where:

$\hat{\mu}_A$ = maximum growth rate for autotrophic biomass, d^{-1}
b_A = specific decay rate of autotrophic biomass, d^{-1}
S_{NO} = oxidised N concentration, $mg \cdot \ell^{-1}$
S_{NO0} = initial concentration of oxidised N, $mg \cdot \ell^{-1}$
t = time, d
Y_A = overall yield coefficient of autotrophic biomass, g cell COD(g oxidised N)$^{-1}$
X_{A0} = initial concentration of autotrophic biomass, $mg \cdot \ell^{-1}$

This equation is often simplified into a simpler linear logarithmic form for the calculation of the corresponding $\hat{\mu}_A - b_A$ value. Sözen et al. (1996; 1997) have shown that the simplified linear expression was not always mathematically justifiable and they have proposed a "curve fitting" approach for the same experimental set-up with rearranging Eq. (1) into:

$$(S_{NO} - S_{NO0})k + 1 = e^{at} \quad (2)$$

where:

$$k = \frac{Y_A}{X_{A0}} \frac{\hat{\mu}_A - b_A}{\hat{\mu}_A} \quad \text{and} \quad a = \hat{\mu}_A - b_A$$

This expression, non-linear in terms of **k** is then solved using the undimensional Fibonacci technique (Wilde, 1964) which computes the $\hat{\mu}_A - b_A$ value with the highest correlation coefficient, using all the experimental data and also selecting the optimum **k** value within a preselected interval. Then, the corresponding $\hat{\mu}_A$ value is calculated, using a default value of 0.05 d^{-1} for b_A (Sözen et al., 1996), as no specific procedure has so far been proposed for the experimental determination of the endogenous decay rate of the autotrophs.

Results and discussion

Studies on nitrification kinetics were carried out as part of a comprehensive survey for the characterisation, COD fractionation and biological treatability of tannery wastewaters (Orhon et al., 1998, 1999b). It basically covered, in the first part, the experimental assessment of the maximum specific growth rate, $\hat{\mu}_A$, applicable to biological treatment of tannery wastewaters and in the second part, the investigation of inhibition effects of selected pollutants on the magnitude of $\hat{\mu}_A$.

Assessment of $\hat{\mu}_A$ for tannery wastewaters

The maximum specific growth rate of nitrifiers, $\hat{\mu}_A$, was experimentally determined for 5 different tannery wastewater samples collected over a period of 6 months covering the entire range of

TABLE 4
CHARACTERISATION OF TANNERY WASTEWATERS

Run No.	COD mg·ℓ$^{-1}$		TKN mg·ℓ$^{-1}$		NH_4^+-N mg·ℓ$^{-1}$	Total P mg·ℓ$^{-1}$	Alkalinity mg·ℓ$^{-1}$ $CaCO_3$	SS mg·ℓ$^{-1}$	VSS mg·ℓ$^{-1}$	S^{2-} mg·ℓ$^{-1}$	Total Cr mg·ℓ$^{-1}$	Cl^- mg·ℓ$^{-1}$	pH
	Total	Soluble	Total	Soluble									
1	2150	1335	246	200	177	7.2	2045	905	515	48	38	6600	7.86
2	2140	1100	196	170	166	7.5	2070	1160	730	45	45	8195	8.1
3	2343	1200	216	178	157	5.9	1200	970	640	17	54	5500	7.4
4	1911	1049	232	189	168	6.5	1050	860	555	37	51.5	6650	8.1
5	2230	1475	250	203	172	4.3	970	679	448	32	66	8095	7.5
Average	2155	1236	228	188	168	6.3	1467	915	578	35.8	50.9	7008	7.79
Max.	2343	1475	250	203	177	7.5	2070	1160	730	48	66	8195	8.1
Min.	1911	1049	196	170	157	4.3	970	679	448	17	38	5500	7.4

different production schemes taking place in the organised district. Analytical results related to the characteristics of samples in terms of relevant parameters are summarised in Table 4. They are quite representative as they reasonably match the average characteristics of the primary effluent of the full biological treatment plant in operation for the Istanbul Organised Leather Tanning Industrial District, where the wastewater samples for this study were sourced (Ates et al., 1997). In fact, the measurements reflect a typical tannery primary effluent quality, with a COD content slightly over 2 000 mg·ℓ^{-1}, a TKN content of around 230 mg·ℓ^{-1}, predominantly soluble after settling, total chromium and sulfide concentrations of 50 and 35 mg·ℓ^{-1} respectively, high alkalinity with a resulting pH of around 8.0 and chloride concentrations in the range of 8 000 to 10 000 mg·ℓ^{-1}, due to chemicals used in leather processing.

For investigating the inhibition of the activity of nitrifiers, the adopted approach was first to remove to the extent possible, pollutants likely to have an inhibitory effect, and then to add desired doses of selected chemicals before the experimental assessment of $\hat{\mu}_A$. For this purpose, the samples were subjected to chemical settling using both alum ($Al_2(SO_4)_3$.18 H_2O) and iron salts ($FeSO_4$, $FeCl_3$) as coagulants together with a suitable anionic polyelectrolite. pH was adjusted by appropriate addition of lime. Chemical treatment was observed to produce for all samples an effluent with a COD concentration of around 1 000 to 1 100 mg·ℓ^{-1}, a suspended solids concentration less than 200 mg·ℓ^{-1}, a sulphide concentration less than 30 mg·ℓ^{-1}, together with an almost complete removal of total chromium (Ates et al., 1997).

The experimental data were evaluated, as outlined in Table 5, using the procedure proposed by Sözen et al. (1996) for the assessment of $\hat{\mu}_A - b_A$ for tannery wastewaters. The effect of initial nitrifiers biomass was investigated by running three parallel batch reactors fed with sample No. 2 at 20°C. Each reactor was initially seeded with a different biomass concentration of 200, 300 and 400 mg·ℓ^{-1} taken from a nitrifying mixed culture sustained at steady state with the same wastewater at a sludge age of 20 d. The change in the N_{OX} concentration in the reactors was monitored for seven days with daily samples as shown in Fig. 1. The evaluation of the N_{OX} profiles on the basis of the adopted procedure clearly indicated that the magnitude of the initial biomass, within the range selected for the experiments, did not affect the reliability of the experiments; consistent $\hat{\mu}_A - b_A$ values of 0.34 to 0.36 d^{-1} were obtained for sample No. 2, regardless of the amount of initial biomass seed.

The maximum specific growth rate of nitrifiers was determined for tannery wastewater samples subjected to both plain and chemical settling. As summarised in Table 5, $\hat{\mu}_A - b_A$ levels for the plain settled effluent at 20°C were observed to remain in the range of 0.25 to 0.36 d^{-1}, with an average value of 0.32 d^{-1}. This value is appreciably lower than the range of 0.45 to 0.80 d^{-1} suggested in the literature for domestic sewage at the same temperature (Ekama and Marais, 1984; Lesouef et al., 1992; Orhon et al., 1994; Henze et al., 1995) but it is of the same magnitude with the average $\hat{\mu}_A - b_A$ level of 0.38 d^{-1} reported by Sözen et al. (1996), characterising Istanbul domestic sewage, generated from the region which also houses the Istanbul Organised Leather Tanning Industrial District investigated in this study.

Two different sets of experiments (Runs 3 and 5), conducted also at 20°C, using chemical settling effluents yielded an average level of 0.42 d^{-1} for the same kinetic coefficient. This value is around 25% higher than the one associated with the plain settled wastewater, reflecting the appreciable inhibitory effect of particulate pollutants removed by means of chemical settling.

TABLE 5
ASSESSMENT OF $\hat{\mu}_A - b_A$ FOR TANNERY WASTEWATERS

Run No.	Initial Biomass (mgVSS·ℓ^{-1})	Temperature (°C)	$\hat{\mu}_A - b_A$ (d^{-1})		
			PS*	CS*	NH_4Cl
1	200	18 – 20	0.25	-	-
2	200	18 –20	0.34	-	-
	300	18-20	0.36	-	-
	400	18-20	0.36	-	-
3	300	20	0.32	0.43	1.0
4	300	10	0.10	0.10	0.43
5	300	20	-	0.40	0.95
		10	-	0.11	0.50

* PS: Primary settling CS : Chemical settling

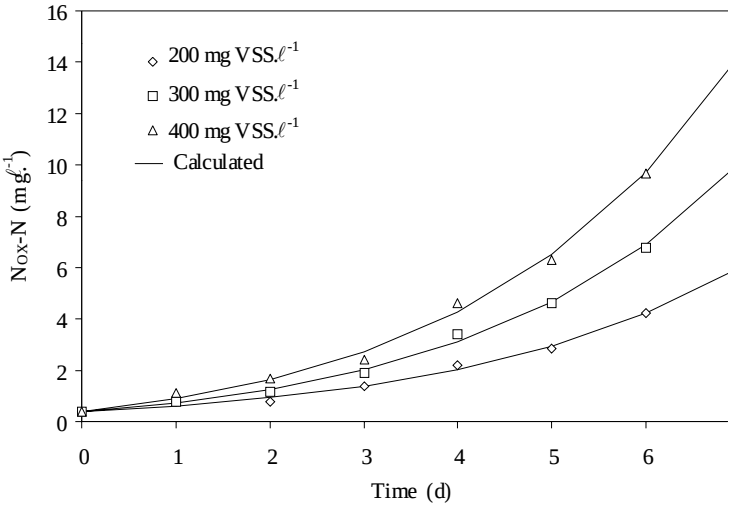

Figure 1
Effect of initial biomass concentration on N_{ox} profiles

As most biological reactions, nitrification kinetics are generally influenced by temperature and the most pronounced effect of temperature is commonly observed on the maximum specific growth rate, $\hat{\mu}_A$ and the endogenous decay coefficient, b_A. The adopted experimental procedure allows for the assessment of the overall temperature effect on $\hat{\mu}_A - b_A$. As this parameter is quite specific to the wastewater treated, this effect was evaluated in this study on the basis of additional experiments performed at 10°C, estimated to be the critical wastewater temperature in winter for the design of the biological treatment systems in the region where the industrial district is located. As illustrated in Fig. 2, the average value of $\hat{\mu}_A - b_A$ at 10°C was observed to drop to 0.10 d^{-1}, less than one third of the level associated with 20°C. Similar experimental studies in the literature suggest that the effect of temperature on $\hat{\mu}_A$ may be evaluated, by an Arrhenius type of an equation, in the range of 7 to 30°C:

$$\hat{\mu}_{AT} = \hat{\mu}_{A20}\theta^{T-20} \qquad (3)$$

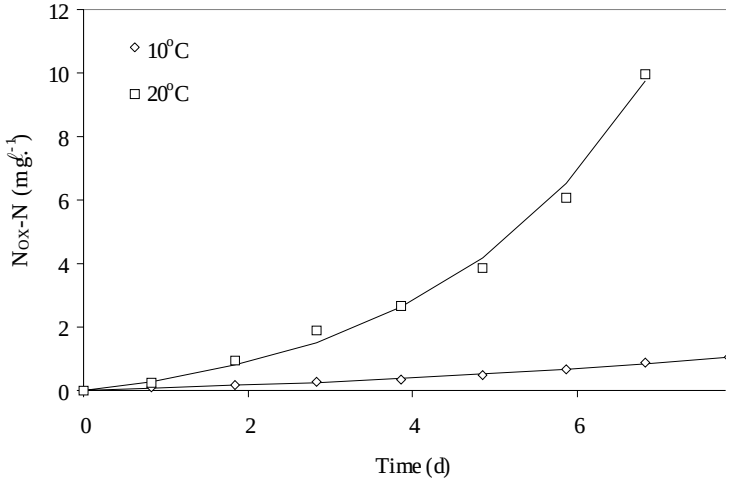

Figure 2
Effect of temperature on observed N_{ox} profiles for chemically settled wastewater (Run 5)

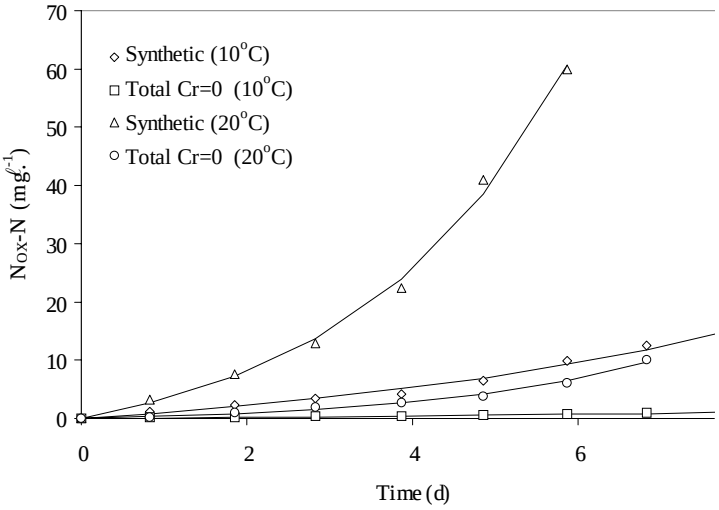

Figure 3
Difference between N_{ox} profiles generated by synthetic waste and chemically settled tannery wastewater at 20 and 10°C

TABLE 6
THE EFFECT OF TOTAL CHROMIUM ON THE GROWTH OF NITRIFIERS

Run No.	Temperature (°C)	$\hat{\mu}_A - b_A$ (d^{-1})				
		NH_4Cl	CS*	Total chromium		
				15 mg·ℓ⁻¹	30 mg·ℓ⁻¹	45 mg·ℓ⁻¹
3	20	1.0	0.43	0.39	0.35	0.34
5	20	0.95	0.40	0.35	0.30	0.29
	10	0.5	0.11	0.10	0.09	0.09

* CS : Chemical settling

The results listed in Table 5 verify the above expression with a temperature coefficient, θ, of 1.127, slightly higher than the range of 1.08 to 1.123 reported for domestic sewage (Ekama and Marais, 1984; Böhnke, 1989; Nowak and Svardal, 1990; Henze et al., 1995; Sözen et al., 1996).

Inhibition of selected pollutants on nitrification kinetics

Tannery wastewaters are likely to incorporate a wide range of different components exhibiting inhibitory or toxic effects to biological treatment and especially to nitrification. In this context, it is of great practical importance to assess whether the experimentally determined value of $\hat{\mu}_A - b_A$ is intrinsic to the wastewater or affected by inhibition. Recently, Nowak et al. (1994) operated batch reactors with synthetic waste devoid of inhibitors, parallel to reactors fed with the wastewater to be tested, to evaluate the existence and the extent of inhibitory effects. In this study, a similar test was carried out on three different runs (Runs 3, 4 and 5) where parallel batch reactors were fed with tannery effluents and synthetic waste containing, as previously described, only NH_4Cl and the nutrient solution. The experiments were conducted both at 20 and 10°C. Reactors run with synthetic waste were initially inoculated with the same amount of biomass (300 mg VSS·ℓ⁻¹), previously acclimated to tannery wastewaters. Results in Table 5 show a significant difference between synthetic waste and tannery wastewater; while synthetic waste reactors produced an $\hat{\mu}_A - b_A$ value of around 1.0 d^{-1} at 20°C, its counterpart was calculated as 0.43 d^{-1} with the chemically settled and 0.32 d^{-1} with the plain settled tannery effluent reactors. As illustrated in Fig. 3, these values provide a clear indication for the strong inhibitory character of tannery wastewaters for nitrification. This character appears to be slightly improved by means of chemical settling. At 10°C, a $\hat{\mu}_A - b_A$ value of 0.5 d^{-1} was calculated for the synthetic waste, with a corresponding θ coefficient of 1.072 for the temperature (Eq. (3)), if applicable.

Inhibition effect of chromium

A particular feature of the tannery wastewater is the trivalent chromium content, both in soluble and particulate nature, depending on the chemical equilibrium sustained in the treatment units. The total chromium concentration of the primary settling effluent may be in the range of 40 to 65 mg·ℓ⁻¹ as indicated in Table 4, and this level should be considered high enough to exert a significant inhibitory effect on nitrification.

The inhibition effect of total chromium was experimentally evaluated with four parallel aerated batch reactors. Chemical settling was used as a pretreatment for the preparation of samples practically devoid of chromium. The first reactor was started with this sample alone and the other reactors with the same sample supplemented with increasing doses of total chromium in the range of 15 to 45 mg·ℓ⁻¹. It should be noted that the latter approximates the chromium content of the plain settled tannery wastewater. Results on two sets of experiments (Runs 3 and 5) are outlined in Table 6, showing a gradual decrease in $\hat{\mu}_A - b_A$ values, from 0.42 d^{-1} for the sample with no chromium to 0.32 d^{-1} for the sample with a total chromium addition of 45 mg·ℓ⁻¹. An interesting observation is the

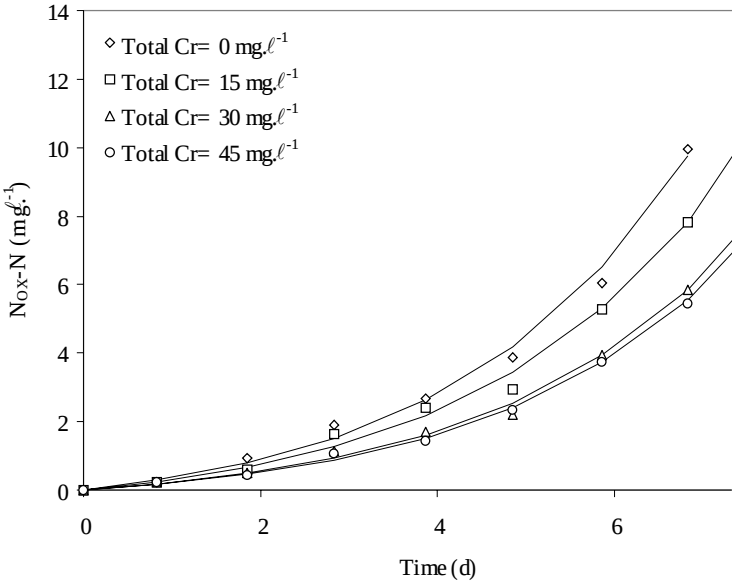

Figure 4
Effect of total chromium on observed N_{ox} profiles at 20°C (Run 5)

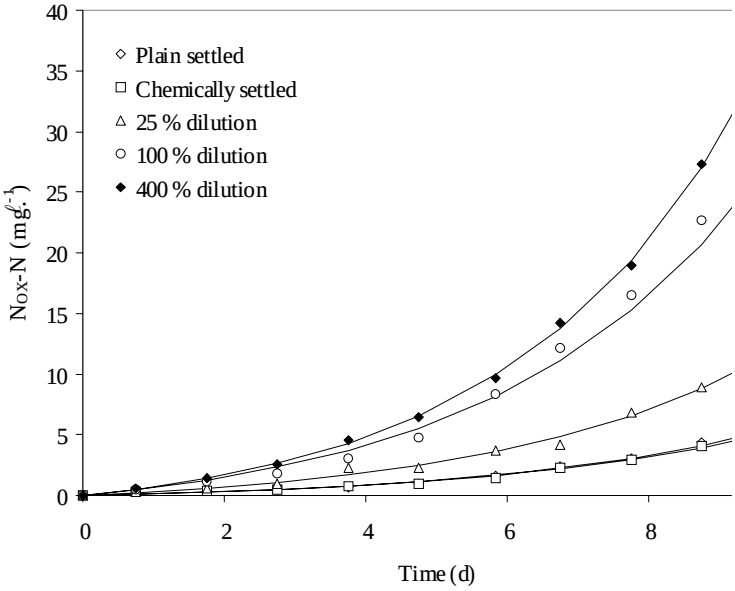

Figure 5
Effect of decrease in chloride concentration by dilution on observed N_{ox} profiles (Run 4)

TABLE 7
THE EFFECT OF Cr^{3+} ON THE GROWTH OF NITRIFIERS

Run No.	Temperature (°C)	$\hat{\mu}_A - b_A$ (d^{-1})				
		NH_4Cl	CS*	Cr^{3+}		
				1.0 mg·ℓ$^{-1}$	2.0 mg·ℓ$^{-1}$	3.0 mg·ℓ$^{-1}$
3	20	1.0	0.43	0.32	0.29	0.27
5	20	0.95	0.40	0.29	0.25	0.22
	10	0.5	0.11	0.10	0.09	0.09

* CS : Chemical settling

fact that 0.32 d^{-1} is practically the $\hat{\mu}_A - b_A$ value previously associated with the plain settled tannery wastewater, indicating that the basic difference between the inhibitory character of chemical settling and plain settling is governed by the removal of chromium. Table 6 also lists the $\hat{\mu}_A - b_A$ values specifically determined for the synthetic waste in conjunction with the same experimental runs. The effect of total chromium addition on observed N_{OX} profiles at 20°C (Run 5) is shown in Fig. 4**.** Comparison of the results displayed in Table 6 provides experimental proof that the inhibitory effect of total chromium is minor with respect to other unidentified factors inherently present in tannery wastewaters. The findings of the same experiment conducted at 10°C provide a stronger support for this argument, as lowering the temperature appears to be a significant factor for the attenuation of chromium inhibition.

It can always be argued that total chromium is not a good parameter in relation to inhibitory effects, mainly because of the chemical balance and especially pH values of 8.0 to 8.5 sustained in reactors treating tannery wastewaters. The majority of the chromium content is likely to be in particulate form, attached to biological flocs and inhibition better relates to the free trivalent chromium concentration in the bulk solution. Experimental surveys show that the latter rarely exceeds 3.0 mg·ℓ$^{-1}$ even in the primary settling effluent (Kabdasli et al., 1993; Ates et al., 1997). To test the possible inhibitory effect of the free trivalent chromium in the bulk solution on nitrification, the same experimental set-up was repeated using three reactors operated with Cr^{+3} contents adjusted in the range of 1.0 to 3.0 mg·ℓ$^{-1}$. The results, outlined in Table 7, exhibit a similar trend as the ones associated with the total chromium experiments, with the exception of slightly higher inhibitory effects, resulting in lower $\hat{\mu}_A - b_A$ values.

Inhibition effect of chloride

The experimental data presented above indicate a significant inhibitory effect on nitrification, remaining after chemical treatment. The high chloride content of tannery wastewaters, observed to fluctuate between 6 000 to 10 000 mg·ℓ$^{-1}$ in this study, is considered as one of the factors likely to produce such an adverse effect (Dahl et al., 1996). One set of experiments was designed to test this effect, at 10°C where the inhibition is most pronounced, by running four parallel aerated batch reactors, the first one started with the undiluted sample and the others with three different dilutions of a chemically treated tannery wastewater (Run 4). The chloride concentration in this wastewater sample was measured as 6 650 mg·ℓ$^{-1}$, and it was reduced successively to 5 000, 3 325 and 1 660 mg·ℓ$^{-1}$. The results are presented in Table 8, together with the ones related to plain settled effluent and the synthetic waste, all initially inoculated with the same nitrifying biomass. As shown by these results also illustrated in

TABLE 8
THE EFFECT OF CHLORIDE ON THE GROWTH OF NITRIFIERS

Run No.	Temperature (°C)	Sample type	Cl^- (mg·ℓ$^{-1}$)	$\hat{\mu}_A - b_A$ (d^{-1})
4	10	NH_4Cl^{-1}	-	0.43
		Plain settled eff.	6 650	0.10
		Chemically settled eff.	6 650	0.10
		% 25 dilution	5 000	0.18
		% 100 dilution	3 325	0.27
		% 400 dilution	1 660	0.31

Fig. 5, the chloride content was observed to exert a significant inhibitory action, illustrated by the positive effect of dilution which increased the $\hat{\mu}_A - b_A$ value from 0.10 d^{-1} in the undiluted sample, gradually to 0.27 d^{-1} at a chloride concentrations of 3 225 mg·ℓ$^{-1}$ and to 0.31 d^{-1} at 1 660 mg·ℓ$^{-1}$. It should be noted that a $\hat{\mu}_A - b_A$ of 0.31 d^{-1} is reasonably close to 0.43 d^{-1} characterising the synthetic waste at the same temperature. Another point of interest is the fact that chemical settling is not likely to affect the Cl^{-1} content of the sample so that the plain settled effluent test displayed on Table 8 was carried out with a chromium level inherently associated with the tannery wastewater, while the test conducted on chemical settled effluent did not contain any chromium. The obtained $\hat{\mu}_A - b_A$ results provide further proof that chromium inhibition is minor compared to Cl^{-1} inhibition.

Conclusions

On the basis of the experimental findings presented and evaluated in the preceeding sections, the following issues may be outlined as the concluding remarks of this study:

The procedure proposed by Sözen et al.(1996) for the experimental assessment of the nitrification kinetics for tannery wastewaters yielded accurate $\hat{\mu}_A - b_A$ values both at 20 and 10°C, for the entire range of data considered for evaluation.

The average value of the rate coefficient $\hat{\mu}_A - b_A$ characterising nitrification at 20°C was calculated as 0.32 d^{-1} for plain settled tannery wastewaters. This value dropped to 0.1 d^{-1} at 10°C, with a corresponding average temperature coefficient, θ, of 1.127. Parallel studies carried out using a synthetic waste solution with no inhibitory or toxic compounds resulted in significantly higher $\hat{\mu}_A - b_A$ values (1.0 d^{-1} and 0.5 d^{-1} at 20°C and 10°C respectively) leading to conclude that tannery wastewaters after plain settling involve components severely inhibiting nitrification.

Chromium was observed to be partly responsible for the inhibitory effect, inducing around a 25 to 30% decrease in the $\hat{\mu}_A - b_A$ value, for a total chromium addition of 45 mg·ℓ$^{-1}$ and a Cr^{+3} level of 3 mg·ℓ$^{-1}$. Experimental results indicate that the basic difference between the inhibitory character of chemical settling and plain settling is governed by the removal of chromium.

Chloride, inherently present in tannery wastewaters was identified as the major inhibitor, exerting a significant inhibitory action, illustrated by the positive effect of dilution which increased the $\hat{\mu}_A - b_A$ value at 10°C from 0.10 d^{-1} in the undiluted sample, gradually to 0.27 d^{-1} with 100% dilution and to 0.31 d^{-1} with 400% dilution. This inhibitory effect, as it is associated with chloride, cannot be suppressed by conventional treatment.

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