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TREATMENT OF TANNERY WASTEWATER IN A SEQUENCING BATCH REACTOR

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ABSTRACT

The aim of the research was to study the treatability of tannery wastewater by a sequencing batch reactor (SBR) compared with a continuous flow full scale reactor. The experimental work presented in this paper was carried out on a laboratory scale anoxic-aerobic SBR fed with tannery wastewater coming from a full scale continuous flow treatment plant located in S. Miniato (Pisa, Italy). After a long acclimation period, a complete and stable nitrification has been developed. The denitrification was always performed without any additional carbon source with good results when influent COD/TKN ratio was higher than 8 and with a higher rate compared to that obtained in the continuous plant. When high effluent nitrate occurred, it was due only to stoichiometric (not kinetic) limitations. The organic substrate removal occurred mainly during the anoxic period and a high effluent COD (refractory) was often present at the end of the process. This research has shown the suitability of the industrial wastewater (particularly tannery wastewater) treatment by SBR because of its several advantages compared to the continuous reactors: i.e. a higher versatility and the possibility to work with higher loads (smaller volumes), by selecting, through the cyclic concentration gradients, a biomass resistant to the presence of inhibiting substances (often encountered in industrial wastewaters).

KEYWORDS

Industrial wastewater; nitrification/denitrification; sequencing batch reactor; tannery wastewater.

INTRODUCTION

The application of biological processes to industrial wastewater treatment still encounters some difficulties mainly due to the presence of inhibiting and/or biorecalcitrant substances. Usually these difficulties are overcome by adopting completely mixed reactors (i.e. low conversion rates), low organic loading rates (i.e. large reactor volumes) and chemical-physical pre- or post-treatments. However, these solutions involve high costs, high sludge production, and high reagent consumption. In particular, tannery wastewater treatment is affected by:

- the presence of substances inhibiting nitrification/denitrification;
- the need to add an external source of a readily biodegradable COD to sustain denitrification, also due to the high fraction of slowly or non biodegradable COD;
- a high effluent COD at the end of the process.

The purpose of this research was to investigate the suitability of sequencing batch processes to tannery wastewater treatment (Irvine and Ketchum, 1989; Artan *et al.*, 1996). It was assumed that, also in the presence of inhibitors, an SBR can be operated with good nitrogen and organic carbon removal at a higher load than a completely mixed reactor (CFSTR). As a matter of fact, it was assumed that the cyclic concentration gradients which the biomass is exposed to in a SBR allows the selection and enrichment of the particular species more able to perform the biological processes required (in particular nitrification and denitrification) in the presence of inhibiting substances, so overcoming their negative effects. Through this particular selection/enrichment it is possible to use a batch process (advantageous from a kinetic point of view) instead of a continuously fed one even in the presence of inhibitors.

METHODS

The experimental work was performed in a 5 l laboratory scale SBR working through 4 cycles each day, with each cycle lasting six hours and consisting of a 1.5 hour anoxic phase, a 3.5 hour aerobic phase, and a 1 hour settle. The reactor was continuously mixed during both the anoxic and aerobic phases. The oxygen was supplied during the aerobic phase by blowing air from the bottom through a pore stone. The temperature was maintained at 20°C by a circulating water bath. The SBR was operated through software connected to a personal computer, in such a way that fill, draw and sludge waste pumps, mixing and aeration were controlled and started/stopped at prefixed times. Moreover, pH, ORP and oxygen concentration were measured continuously throughout the process. Oxygen concentration was controlled by intermittent aeration in order to have always a concentration around 2 mg/l during the aerobic phase.

The feed (1.5 l) was given at the beginning of the anoxic phase in 13 minutes and the same volume of supernatant was drawn at the fortieth minute of the settle phase also in 13 minutes. The hydraulic retention time was 0.8 days. The excess sludge was drawn at the end of the aerobic period (75 ml of aerated mixed liquor). The sludge age was 17 days.

The SBR was fed with a real wastewater effluent coming from the tannery industries located in Tuscany (Italy). The wastewater was collected at the real wastewater treatment plant after the chemical-physical pre-treatments and just before being mixed with municipal wastewaters at the inlet of the biological units. In order to simulate such a dilution, the feed to the SBR was obtained by diluting the real wastewater with tap water. To satisfy the metabolic needs of the biomass, phosphorus was also added in order to ensure a concentration of at least 6 mg/l in the feed. The influent so prepared was stored in refrigerator at 4°C and continuously stirred. According to the wide variability of the different batches of wastewater collected, the influent concentration varied in the range 300-1400 mg/l as COD and 50-200 mg/l as TKN.

The sampling and analyzing procedures followed the Standard Methods for the Examination of Water and Wastewater (1995). Twice a week, samples of the influent feed and of the mixed liquor at the end of both anoxic and aerobic phases were drawn. Dissolved components were measured after immediate filtration of samples on GF/C filters. On the influent feed, parameters determined were COD, TKN, NH_3-N, P, and chloride. At the end of the anoxic and aerobic phases, parameters analyzed were COD, TKN, and NO_x-N, all of them on filtered samples. At the end of the aerobic phase, NH_3-N and P were also measured on filtered samples as well as MLSS and MLVSS on the mixed liquor. All COD measurements were corrected according to the chloride concentration in the feed (Pettine *et al.*, 1992). Periodically, mass balances for COD and nitrogen were calculated by also measuring total COD, TKN and NO_x-N of the effluent and excess sludge. Kinetic studies of denitrification and nitrification were periodically performed by sampling several times the mixed liquor during the anoxic and aerobic phase respectively. In both cases, NO_x-N, NH_3-N and occasionally COD were determined on filtered samples. All the calculations about the denitrification rates or COD removal rates were made taking into account the mass of nitrate or COD removed (i.e. the product of volume x concentration) in order to avoid any interference of dilution during feed.

OUR (Oxygen Uptake Rate) in the aerobic phase was automatically measured by recording the decrease of oxygen concentration versus time in the absence of aeration. Readily biodegradable COD measurements were also performed according to the physical-chemical method (Mamais *et al.*, 1993).

RESULTS AND DISCUSSION

The operating strategy described in the previous section has been chosen among different alternatives tested in the first 100 days of experimentation. During the next 150 days of experimentation nitrite concentration at the end of the aerobic phase was quite high while nitrate concentration was still low, probably because the most sensitive *Nitrobacter* spp. (Abeling and Seyfried, 1992), carrying out the nitratation, were not completely acclimated yet. Then nitrite concentration decreased progressively with time while nitrate nitrogen started to increase. After day 300 a complete nitrification to nitrate, with very low nitrite at the end of the aerobic phase, occurred.

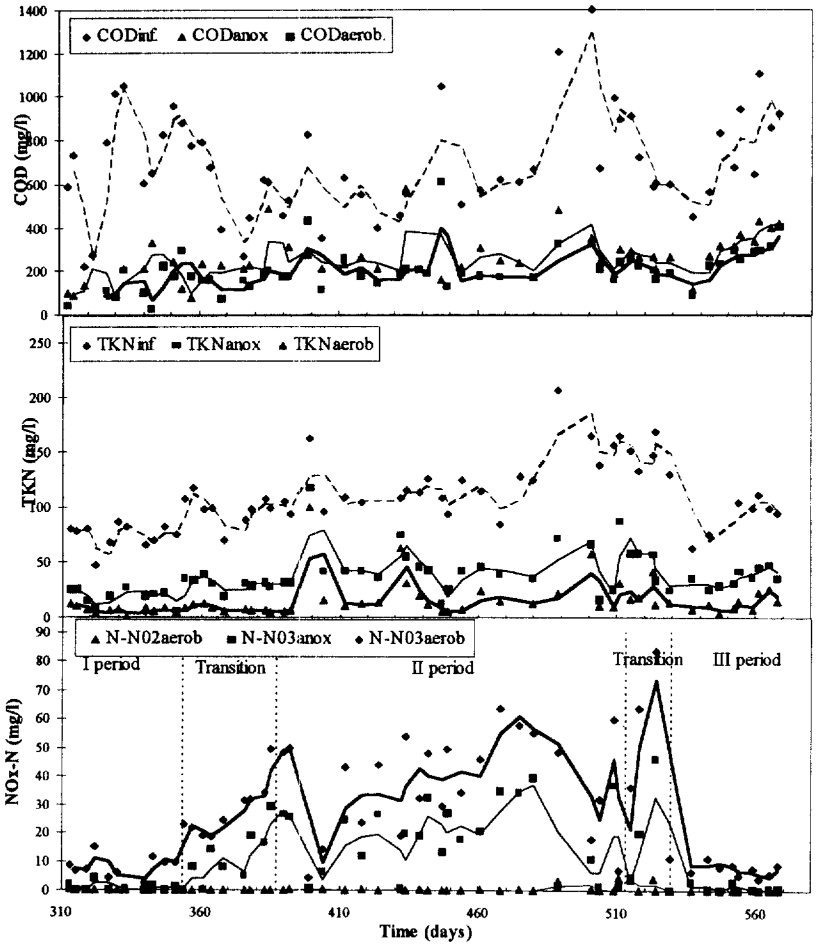

Figure 1. COD, TKN and NO_x-N time profiles throughout the experimental period (values at the end of anoxic and aerobic phases were measured on filtered samples).

The results presented in this paper refer to the following period, after the acclimation of *Nitrobacter* spp. had completely occurred. Figure 1 shows COD, TKN and NO_x-N time profiles in the influent and at the end of the aerobic and anoxic phases. COD and TKN profiles at the end of both aerobic and anoxic phases are quite constant throughout the experimental period, in spite of the wide variability in the influent. Conversely nitrate profiles at the end of both phases are widely variable with time and a correspondence between them is also present. Three main periods characterized by a stable behaviour, with intermediate transition periods, can be recognized:

- I period, from day 313 to day 353, with very low nitrate concentration at the end of the anoxic phase and corresponding low nitrate concentration at the end of the aerobic phase;
- II period, from day 388 to day 513, with high nitrate at the end of both anoxic and aerobic phases;
- III period, after day 530, similar to the first period

Table 1 shows the average values of COD, TKN and NO_x-N in the influent, at the end of the aerobic phase and at the end of the anoxic phase in the three periods above presented. These values indicate that in the second period the influent COD and TKN were lower and higher, respectively, than in the other two periods with better performances. Indeed, Table 2 shows that both influent COD to TKN ratio and the effectively available COD to TKN ratio (i.e. (CODi-CODaer)/TKNi) were quite lower during the second period. However TKN removed was quite high leading to higher nitrate to be denitrified. Even though this higher denitrification is confirmed in Table 2, nitrate concentration at the end of the aerobic phase remained still high.

Table 1. Mean values of COD, TKN and NO_3-N concentration during the different periods

Period	Days	COD (mg/l)			TKN (mg/l)			NO_3-N (mg/l)	
		Influent	anox	aerobic	Influent	anox	aerobic	anox	aerobic
I	313-353	701	151	121	74.1	18.7	6.5	0.97	8.1
II	387-513	679	271	226	124.1	46.6	22	18.8	38.2
III	530-568	777	328	267	91.8	36.1	12.5	0.88	7.1

Table 2. Mean values of the main process parameters during the different periods

Period	Days	ΔCODanox (mg/l)	ΔCODaer (mg/l)	ΔTKN (mg/l)	Ndenitrified (mg/l)	CODi/TKNi	(CODi-CODaer) / TKNi	ΔCODanox / Ndenitrified
I	313-353	160	42	69	4.5	10.2	8.8	36.9
II	387-513	96	49	108	9	5.3	3.7	10.3
III	530-568	89	60	78	4.1	8.3	5.6	22

Figure 2, presenting individual data throughout the periods, clearly shows that complete denitrification occurred for influent COD/TKN values higher than 8, while at lower values of this ratio, nitrate concentration at the end of the aerobic phase was inversely related to it. Thus the incomplete denitrification leading to a high nitrate concentration at the end of both phases during the II period is explained by the lack of COD to sustain the denitrification, i.e. by stoichiometric factors.

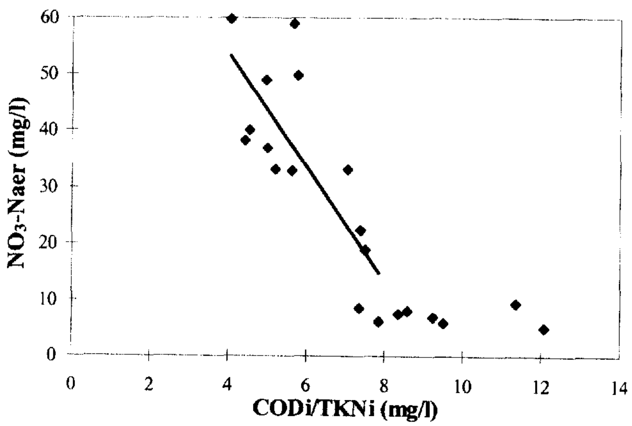

Figure 2. Comparison between influent COD/TKN and nitrate concentration at the end of the aerobic phase.

On the other hand a high residual COD was always present at the end of the anoxic phase (see table 1), revealing that the lack of organic substrate for denitrification was mainly due to the slowly biodegradable or refractory nature of this COD. Readily biodegradable COD fraction of the influent tannery wastewater was only 12%.

Indeed, from Figure 3a, two different kinetic behaviours for nitrate removal are identifiable: in the initial step nitrate removal occurred at a higher rate while in the following step the removal rate was much lower. Similar two-step profiles were obtained for COD (not reported) so indicating the relationship between nitrate and COD removal rates: Figure 4 shows a typical linear relationship between COD and NO_3-N removed during an anoxic phase. From these typical profiles the ratios $(COD/NO_3\text{-}N)_{removed}$ were calculated: the resulting values (as shown in Table 2) are quite higher than the stoichiometric ones probably due to sorption and/or accumulation phenomena. Because at the change of removal rates residual COD was still high, this residual COD was confirmed to be slowly or non biodegradable.

Figure 3b shows that, when effluent nitrate concentration was low, the denitrification at the highest initial rate was sufficient to remove nitrate completely.

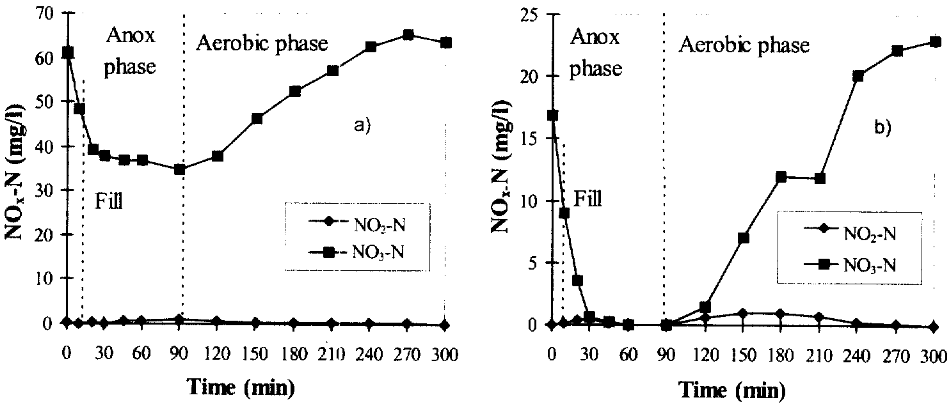

Figure 3. Typical NO_x-N time profiles for low (3a) and high (3b) denitrification performances.

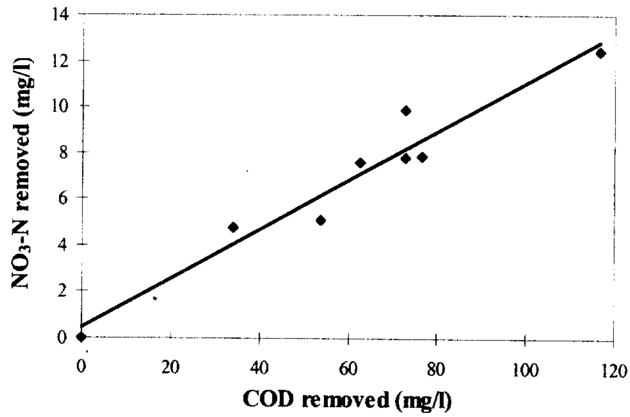

Figure 4. Relationship between nitrate and COD removed during the anoxic phase.

The absence of additional kinetic effects (inhibitions) in the II period is also demonstrated by Table 3 which clearly shows that the average denitrification rates (either calculated at the beginning of the anoxic phase only, i.e. the maximal ones, or calculated throughout the phase) were higher in the II period than in the other two.

Figure 3 also shows the good performance of nitrification in the aerobic phase. After a very long period of acclimation/selection, nitrification rates throughout the following experimentation periods, as shown in table 4, were comparable and even higher than those cited in the literature (i.e. 0.04 ÷ 0.17 mg NH_3-N/mg VSS·d) for municipal wastewater (Beccari *et al.*, 1996).

Table 3. Denitrification rates during the different periods

Period	Days	MLVSS (mg/l)	Denitrification rates	
			(mg NO_3 - N)/(g $_{VSS}$·d) (throughout anox phase)	(mg NO_3 - N)/(g $_{VSS}$·d) (maximum slope)
I	313-353	3949	24	83
II	387-513	2785	96	281
III	530-568	2536	51	167

Table 4. Nitrification rates during the different periods

Period	Days	MLVSS (mg/l)	Nitrification rates	
			(mg NH_3 - N)/(g $_{VSS}$·d) (throughout aerobic phase)	(mg NH_3 - N)/(g $_{VSS}$·d) (maximum slope)
I	313-353	3949	14	34
II	387-513	2785	64	120
III	530-568	2536	11	16

Table 5 shows the COD removal rates (kgCOD/kgVSS·d), the nitrogen removal rates (kgN/kgVSS·d) and the growth yields (mgVSS/mgCOD) for both the laboratory SBR and the full scale continuous plant. It should be noted that the SBR has been run at higher organic loads than the real plant.

Table 5. Nitrogen and COD removal rates and yields for the SBR and the full scale plant

SBR

Period	COD removal rates (kgCOD/kgVSS·d)	N removal rates (kgN/kgVSS·d)	Organic load (kgCODi/kgMLSS·d)	Y (mgVSS/mgCOD)
I	0.19	0.02	0.21	0.60
II	0.19	0.04	0.26	0.62
III	0.24	0.04	0.32	0.47
Total Time	0.21	0.03	0.26	0.56

Full scale plant

Period	COD removal rates (kgCOD/kgVSS·d)	N removal rates (kgN/kgVSS·d)	Organic load (kgCODi/kgMLSS·d)	Y (mgVSS/mgCOD)
1997	0.12	0.009	0.088	0.62

COD and nitrogen removals were always performed at higher rates in the SBR than in the real plant, even though in the latter an external substrate (methanol) is added to allow a better denitrification; growth yields were almost the same for both plants and were calculated on the base of sludge production.

These data confirm the much higher treatment efficiency of the SBR compared to the real plant, even because no external substrate was added to perform a higher rate denitrification, differently from the real plant. Moreover the recycle ratios used in the SBR were much lower than those required in the real plant: i.e. 2.3 and 10-11, respectively.

Finally, throughout the experimentation the activated sludge exhibited good settling properties, with SVI always less than 120 ml/g.

CONCLUSIONS

The experimental work has shown the following advantages arising from the tannery wastewater treatment by the SBR compared to the traditional continuous plants:

- selection of a biomass with high resistance to the inhibiting substances present in the wastewater even at higher organic loads;
- kinetic advantage of SBR leading to higher substrate removal rates;
- better selection of the floc-forming microorganisms in such a way that a settling improvement is gained.

Even though operated at a higher organic load, the process appeared quite robust with respect to COD removal and nitrification, in both cases easily recovering wide variation of influent COD and TKN. Nevertheless residual COD was always high due to the high fraction of organic substances that are practically biorecalcitrant. Preliminary investigation by ultrafiltration has shown that most of these compounds are concentrated in a fraction with a molecular weight between 1000 and 10 000 Daltons and their increase in the effluent could be due either to the hydrolysis of the higher molecular weight fractions contained in the influent or to the formation of Soluble Microbial Products (SMP) by the endogenous biological activity (Boero *et al.*, 1996; Pribyl *et al.*, 1997).

As a consequence, nitrate removal efficiency sometimes suffered from a lack of readily available COD for denitrification. It has been shown that the influent COD/TKN ratio has to be at least 8 w/w in order to obtain an effluent nitrate concentration low enough (at least at the adopted internal recycle ratio). The internal recycle ratio (which for a SBR is given by initial volume to feed volume ratio, V_0/V_F) is an important variable in order to obtain low effluent nitrate concentrations; however in our research it was not increased because the lack of the available COD limited the denitrification potential.
The results obtained suggest continuing the research by investigating:

- the maximum loading acceptable in a periodic process based on SBR;
- the suitability of such a periodic process to tannery wastewaters without chemical-physical pretreatment;
- the suitability of a partial chemical oxidation in order to transform the high residual COD into a biodegradable form, so simultaneously increasing the COD available for denitrification and decreasing the residual COD in the effluent.

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