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COMBINED OXIDATIVE AND BIOLOGICAL TREATMENT FOR SEPARATED STREAMS OF TANNERY WASTEWATER

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ABSTRACT

The biological treatment of the tannery wastewater substreams beamhouse (BH, pre-tanning steps) and tan-yard wastewater (TY, tanning, & wet-finishing process steps) and the application of an oxidative treatment by ozone, followed by a second aerobic treatment are investigated.

Due to the extremely changing quality of the raw wastewater, esp. TY, the biological pre-treatment could not be stabilized all the time and nitrification was sometimes inhibited. Oxidative treatment distinctly improved the aerobic biodegradability of refractory organic compounds and it was found to be optimal in the range of a specific ozone consumption of about 2 g O_3/g DOC_0 for both batch experiments and continuous operating conditions.

Moreover, full nitrification could be established during the subsequent aerobic degradation and the remaining ammonia was completely removed. Summing up, it can be stated that the combined oxidative and biological treatment of BH and TY was effective and ensures the meeting of given COD and ammonia-limits for the direct discharge of this special industrial wastewater into rivers.

KEYWORDS

biodegradability, combined oxidative and biological wastewater treatment, multiple-step treatment, nitrification, ozonation, oxidation products, refractory organics, specific ozone consumption, tannery wastewater

INTRODUCTION

The tanning procedure, as a chain of several batch processes, produces wastewaters which are usually characterized by both high amounts of organic substances (COD, BOD, DOC) as well as high concentrations of inorganic salts like chloride, ammonia, sulphide and sulfate.

Moreover, during the tanning process some chemicals are applied like fungicides (e.g. benzothiazole), vegetable and synthetic tanning agents (e.g. sulphonated phenolic polymers) and dyes, which may cause problems in conventional municipal wastewater treatment (Reemtsma et al. 1993, 1995). For example they may inhibit the nitrification process or pass through biological steps because of their refractory properties (Reemtsma 1997). The COD-contents and pH-values of the process steps show distinct variations (Tab. 1) and after dilution by water during washing procedures these different wastewaters are normally mixed and then treated as full stream wastewater.

Reviews of tannery wastewater treatment are given by Tsotsos (1986) and Daryarpurkar et al. (1989) and some special investigations on inorganics have been carried out, like precipitation of sulphide with Fe II-salts (Szpyrkowics et al. 1991), removal of ammonia with natural ion exchangers (Chmielewska-Horvathova et al. 1992) and recovering and re-use of chromium (III) by solvation with sulphuric acid.

In order to reduce problematic organics, Roszak and Pekala (1983) treated tannery effluents by γ-irradiation and Bilyk and Szpadt (1990) proposed a multiple step treatment including biological treatment, chlorination, sand filtration, activated carbon adsorption and reversed osmosis for re-use in the beamhouse.

Table 1: COD and pH of relevant wastewater producing process steps during the tanning procedure

Sub-stream	Process	pH	COD [ppm]	Applied chemicals	Washing
Beam-house	Pre-soaking	6.8	3,800	chloride, biocides	
	Soaking	8.6	8,400		
	Liming	12.8	26,600	sulphide, lime	1 x
	Deliming Bating	7.1	8,300	ammonia-chloride	
Tan-yard	Pickling Chrome-Tanning	4.1	11,000	sulphuric acid, chloride Chromium III- sulphate bicarbonate, fungicides	1 x
	Neutralization	4.8 - 6.3	1,900 - 3,200		1 - 2 x
	Re-Tanning	4.1 - 6.4	2,200 - 19,700	synthetic and vegetable tanning agents	1 - 2 x
	Dyeing	3.3 - 4.3	22,000 - 53,800	various dyes	2-3 x
	Fat-liquoring	3.6 - 4.0	9,000 - 28,200		1 x
	Fixing	3.5	1,400 - 3,800		1 x

In our case the biological treatment of tannery wastewater from a german tannery (full stream wastewater of all process steps) was first performed in a two step biological treatment plant. Anaerobic and subsequent aerobic treatment led to a significant removal of COD and DOC but still the remaining contents (e.g. COD of 400 to 800 ppm) were not acceptable for direct discharge into rivers and full nitrification could not be established at all (Genschow and Hegemann 1993).

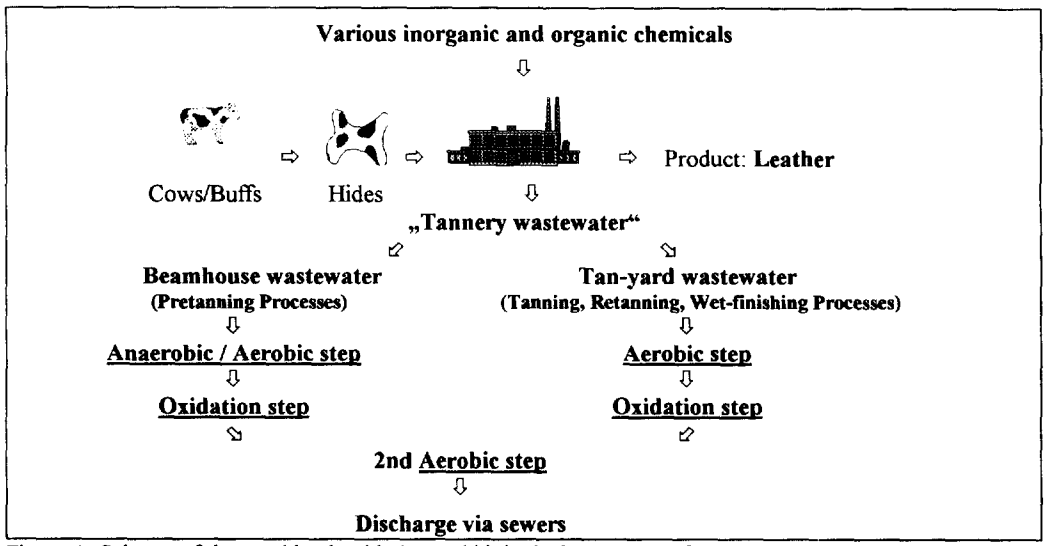

Figure 1: Scheme of the combined oxidative and biological treatment of tannery wastewater substreams

Therefore, two strategies for an optimization were chosen (Fig. 1):

1.) Improvement of the biological pretreatment by dividing the wastewater of all process steps into two substreams: The pretanning process steps (soaking, liming etc.) are combined in the so-called *beamhouse* wastewater (BH) and the tanning, retanning and wet-finishing steps (dying, fatliquoring etc.) contribute to the so-called *tan-yard* wastewater (TY).

2.) Integration of an oxidative step (ozonation) in order to break up the above mentioned refractory or toxic organic substances (e.g. Gilbert 1987, Narkis et al. 1984) and possible nitrification inhibitors, followed by a second aerobic step for the biological degradation of the formed oxidation products.

This paper reports on experiences with the combined oxidative and biological treatment for separated streams of tannery wastewater, especially the treatment of tan-yard wastewater.

EXPERIMENTAL

Design of the lab scale plant

Both, beamhouse and tan-yard wastewater were treated aerobically, oxidative and subsequently aerobically with identical reactor systems (Fig. 2). Only the beamhouse wastewater was pre-treated anaerobically, using a fixed bed column (filled with Raschig rings 35 x 35 mm, total volume: 7.4 l, t_R = 2 d).

The effluent of the following aerobic treatment (CSTR, total volume: 14 l, t_R = 2-4 d) with sludge recirculation (recycle rate 1 to 4) has to be stored (room temperature, darkness), because of the low retention time during the oxidation process (t_R = 1 h).

The ozonation was carried out in a CSTR made of glass (height and diameter 20 cm, total volume 6 l, k_La = 0.38 and 0.73 min^{-1} for ozone and oxygen, rsp.; stirrer: 1,500 rpm). Ozone was produced from technical oxygen (gas flow of 45 l h^{-1}, ozone dose rate = 5 mg ozone l^{-1} min^{-1}, equivalent to an ozone partial pressure of 1,800-1,900 Pa). A computer-aided on-line ozone mass balance allowed the immediate calculation of the applied ozone dose (input - output gas concentration, measured by UV-spectrophotometers) and, taking into account the concentration of ozone in the fluid (detected by an electro-chemical ozone sensor), also of the ozone consumption. For the subsequent aerobic treatment of the stored oxidation effluent (10 °C, darkness) a fixed bed column filled with foam particles for biomass immobilization was employed (total volume: 5 l, with a counter-current external loop t_r = 5 d). During all treatment steps the pH-value was adjusted via an automatic pH-value control apparatus, a more detailed description is given elsewhere (Jochimsen and Jekel 1997).

In the case of batch-ozonation, the identical oxidation reactor operated in batch mode and subsequent aerobic biodegradation was determined according to EN ISO 9888 on estimation of ultimate bio-degradability (stirred 250 ml flasks). Mixed cultures from a municipal wastewater treatment plant were employed as inocculum. Preliminary studies showed the end of degradation after 7 to 10 days (Jochimsen and Jekel, 1994). Hence, the tests on biodegradation were finished after 14 days of incubation. All tests were performed including a reference (aniline) to ensure biomass activity and a poisoned sample for assessing adsorption or precipitation effects on biomass particles. Tests on inhibition of the nitrification (ammonia removal rate) were performed according to EN ISO 9509 (4 h incubation of mixed cultures).

Analytics

All samples were filtered over a 0.45 µm membrane prior to analysis. The COD-concentration was analysed according to DIN 38409 H 41-2. DOC-content was determined with a DOC-analyzer using wet-chemical oxidation including UV-irradiation after persulfate addition (LiquiTOC, Heraeus, Hanau, FRG). Prior to detection of UV-absorbance at a wavelength of 254 nm (Lambda 2, Perkin-Elmer, Überlingen, FRG), the pH of all samples was adjusted to pH 7.5 by dilution with 67 mM phosphate buffer. Ammonia, nitrite and nitrate were detected using the FIA-star system, Tecator, Upsala, Sweden.

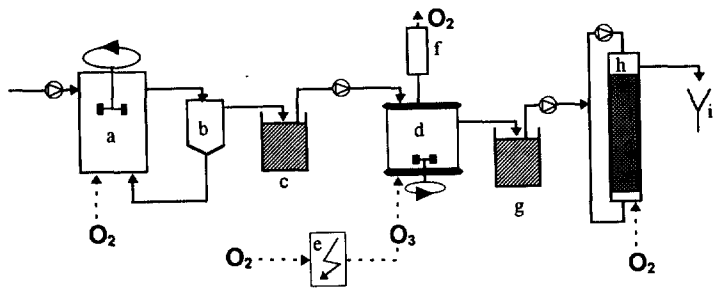

Fig. 2: Scheme of the lab-scale pilot plant
a - 1st aerobic step, CSTR
b - clarifier with sludge recirculation
c, g - storage tank
d - ozone reactor, CSTR
e - ozone generator
f - activated carbon filter
h - 2nd aerobic step: fixed bed column
i - 2nd aerobic effluent

RESULTS AND DISCUSSION

Biological pretreatment of beamhouse and tan-yard wastewater

A biological pre-treatment of tannery wastewater before oxidation is efficient and feasible, because of the high load of easy biodegradable organic compounds like proteins and fatty acids, e.g. due to the hydrolysis processes of the skin structures. The two different streams of tannery wastewater BH and TY were treated in a different way: 1) Beamhouse WW: Anaerobic ⇒ Aerobic ⇒ Oxidation ⇒ Aerobic

2) Tan-Yard WW: Aerobic ⇒ Oxidation ⇒ Aerobic.

The relevant chemical parameters of the separated streams of tannery wastewater and the accompanying effluents after biological treatment (BH: anaerobic/aerobic; TY: aerobic) are displayed in table 2. As typical for tannery wastewater, most parameters show remarkable fluctuations.

Table 2: Relevant parameters of raw tannery substreams beamhouse, BH and tan-yard waste-water, TY and the corresponding effluents of the biological steps (an: anaerobic, ae: aerobic)

Parameter	unit	Beamhouse Waste Water	BH: Aerobic Effluent	Tan-yard Waste Water	TY: Aerobic Effluent
COD	mg/l	3,500 - 5,000	220 - 500	1,500 - 8,000	150 - 2,100
DOC	mg/l	1,000 - 1,500	80 - 150	600 - 2,500	100 - 750
NH_4-N	mg/l	350 - 490	0 - 490	10 - 250	0 - 250
Sulfate	mg/l	300 - 500	550 - 600	1,400 - 2,000	1,400 - 2,000
Sulphide	mg/l	200 - 400	< 0,5	-	-
Cr total	mg/l	-	-	30- 250	1 - 10
Chloride	mg/l	1,000 - 5,000	1,000 - 5,000	600 - 8,000	600 - 8,000
pH		10 - 12	7.8	3 - 4	7.8
retention time t_R	d		an: 3 ae: 2 - 4		ae: 2 - 4

In general, BH-wastewater contains the less toxic chemicals, but has a very basic pH of 11 which needed to be neutralized by addition of carbon dioxide and/or phosphoric acid. The high COD (3,500-5,000 ppm) and a relatively favourable ratio of COD to sulfate seemed to be promising for an anaerobic treatment of BH After 50 to 80 % of COD-removal through anaerobic processes the following aerobic step with sludge recirculation leads to a total COD-removal of up to 85 to 90% (=300-500 ppm). However, full nitrification was often disturbed.

In contrast, the TY-wastewater contains the vast majority of the toxic organics applied during the tanning process. Hence, after neutralization (original pH 4-5) TY was treated aerobically in the same way like BH (activated sludge process). At neutral pH almost all of the Chromium(III) precipitates to the hydroxide form and is simultaneously removed with the activated sludge. After aerobic treatment COD remains at 15 to 20% of initial COD (1,500-8,000 ppm), which is still too high for the direct discharge. Moreover, it can be stated that full nitrification is often disturbed or sometimes could not be established at all.

Oxidation and subsequent biodegradation of tan-yard wastewater

The combined oxidation and subsequent biodegradation makes it necessary to examine the optimal point of oxidative treatment with ozone, because oxidative destruction of the organic matter, as indicated by COD, DOC and UV-removal, is less favourable in the case of further oxidative mineralization of already biodegradable oxidation products. Hence, some experiments in batch mode were performed, in order to evaluate the most favourable conditions. The specific ozone consumption (C_{spec}, unit: g Ozone consumed per g of initial-DOC) allows to compare the effectivity of an oxidative treatment of different types of tannery wastewaters and makes it possible to describe the achieved oxidation effects dimensionless with respect to the needed oxidation time.

Figure 3 shows the degree of oxidative removal of COD, DOC and UV (absorbance at 254 nm) after batch-ozonation. As expected, all parameters increase with elevated values of Cspec, but in a quite different way. The destruction of aromaticity is very effective and only a C_{spec} of 1 g/g is needed to obtain a UV-removal of 40%. Compared to UV and COD-removal the oxidative destruction of DOC is obviously delayed. This phenomenon is due to easily oxidizable organic matter, which can be mineralized only at higher ozone consumptions. Therefore, COD/DOC and UV/DOC-ratios are shifted from 2.4 to 1.5 and from 1.4 to 0.9, respectively at a C_{spec} of 4.4 g O_3/g DOC_0.

Figure 4 illustrates the DOC-removal by subsequent aerobic treatment of the ozonated samples (batch test) and the αDOCsum and αCODsum, summarizing oxidative and subsequent biological DOC and COD-removal, respectively.

On one hand, the oxidative destruction increases with increasing specific ozone consumption. About 50% DOC-removal were obtained at C_{spec} = 4.4 g O_3/g DOC_0. On the other hand, the subsequent biological degradation is most efficient at a specific ozone consumption between 1 to 3 g O_3/g DOC_0. Further oxidation diminishes the degree of biological DOC-removal, as explained above.

As a consequence of these findings, the ozonation of this TY-batch in continuous mode was performed with specific ozone consumptions in the same range.

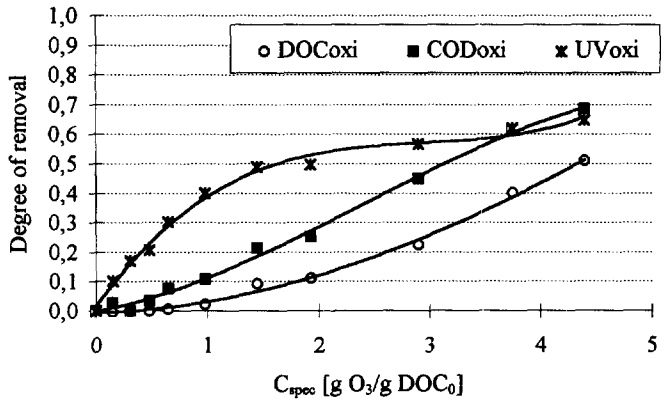

Fig. 3: Degree of oxidative removal of COD, DOC, UV and of Tan-yard wastewater (TY) versus C_{spec} (TY: COD_0 = 450 ppm, DOC_0 = 185 ppm, UV_0 = 258 m^{-1}, referred to the 1st aerobic effluent.).

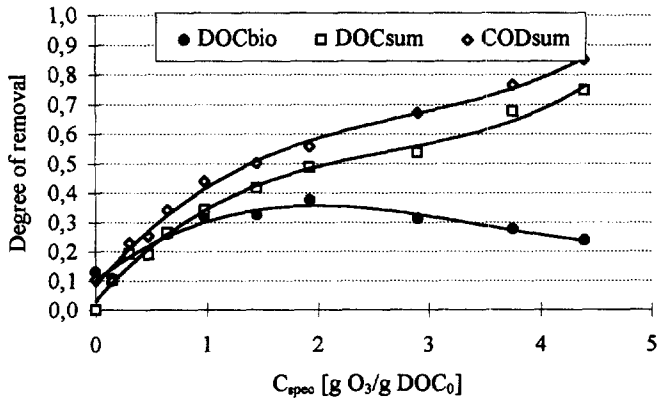

Fig. 4: Degree of biological DOC-removal, αDOCsum and αCODsum of Tan-yard wastewater (TY) versus C_{spec} (initial values see fig. 3).

The COD and DOC - contents of the raw TY-wastewater and the effluents of the first aerobic step, the ozonation and the second aerobic step are given in figure 5. Summarizing the effects on COD-removal it can be stated, that only after the application of C_{spec} = 2,1 g O_3/g DOC_0 the effluent of the subsequent aerobic treatment meets the given limit of 250 ppm COD. According to figure 4, otherwise a specific ozone consumption of C_{spec} > 3.3 g O_3/g DOC_0 must have been applied, in order to reach this COD-limit by sole oxidative treatment.

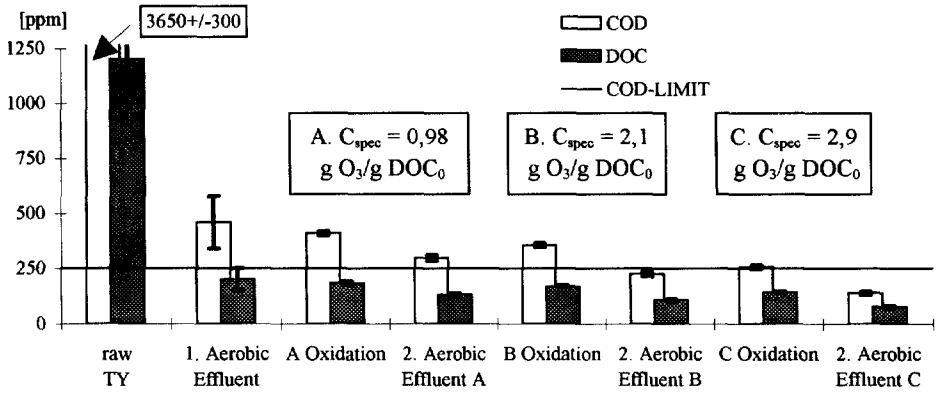

Fig. 5: COD and DOC-contents of raw TY-wastewater and the effluents of the 1st aerobic (t_R = 4 d), oxidative (pH 7, C_{spec} = 1 - 3 g O_3/g DOC_0) and 2nd aerobic (t_R = 5 d) treatment (averaged values at steady state conditions and standard deviations).

Thus, as far as COD-removal is concerned, the biodegradation seems to be suitable for realizing a more economical use of ozone (Jochimsen and Jekel 1996, 1997). Total COD-removal of 95% could be achieved, compared to 83% of the 1st aerobic effluent. Moreover, this batch of TY-wastewater contained a dark black dye, which passed through the first aerobic step (absorbance at 436 nm, colour units: CU = 27 m^{-1}) and then could almost completely be destroyed by chemical oxidation (CU < 2 m^{-1}).

Removal of ammonia by full nitrification

Whereas some authors report on the feasibility of undisturbed biological nitrogen removal from tannery wastewaters (Szpyrkowicz et al. 1991b, Panzer et al. 1981), in this case full nitrification could not be stabilized during the whole period of continuous biological pre-treatment of both BH and TY wastewater. This might be due either to inorganic or organic nitrification inhibitors or even unfavourable conditions for the nitrifying against competing heterotrophic microorganisms (e.g. CSTR with high organic load).

It is known, that high concentrations of chloride and especially sulfate, which are typical compounds of tannery effluents (Tab. 1), may inhibit the nitrification process significantly (Schenk and Hegemann 1995, Vismara 1982). Moreover, it could be shown that the fungicide TCMTB (thiocyanomethylthiobenzothiazole) and its metabolites, acting as a PCP-substitute in the leather industry, are very potent inhibitors of biological ammonia removal (Reemtsma et al. 1995).

Figure 6 shows the results of a short time batch-essay for estimating the inhibition of the ammonia removal rate, using two customary vegetable tannins (Mimosa and chestnut-extracts) and two technical mixtures of synthetic tanning agents (synthetic phenolic polymers), which are often applied in the re-tanning process. Except for the results of *syntan1*, the inhibition of nitrification could distinctly be reduced by ozonation.

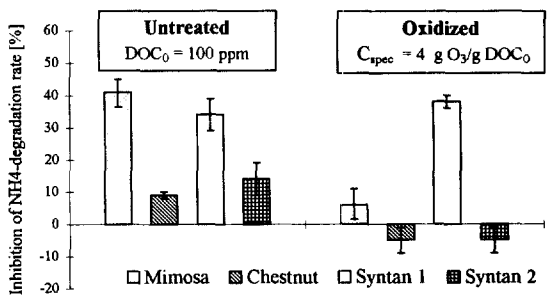

Fig. 6: Inhibition of the biological ammonia-degradation rate by samples of vegetable (mimosa, chestnut) and synthetic tanning agents (syntan 1 and 2) short time batch-essay.

An typical example of another continuously treated tan-yard wastewater (Fig. 7) shows incomplete nitrification, including a temporary accumulation of nitrate up to 30 ppm. The performance of ozonation at neutral pH of 7 does hardly affect the ammonia-concentration, because the formation of nitrate by chemical oxidation occurs only at basic pH of 8 and above. Due to the full nitrification of remaining ammonia established in the subsequent aerobic step, the quality of the effluent changes significantly and thus, the meeting of the ammonia limit of 10 ppm can be ensured.

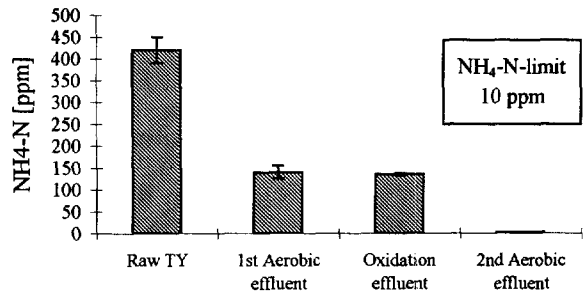

Fig. 7: Ammonia content of Tan-yard wastewater, TY (1st aerobic - t_r = 4 d, oxidative - pH 7, C_{spec} = 1.9 g O_3/g DOC_0 and 2nd aerobic step - t_r = 5 d) COD_0/DOC_0 = 3500/1200 ppm (raw TY-wastewater) Chloride = 3600 ppm, Sulfate = 500 ppm

Like shown in this case, the perfomance of an oxidative treatment of TY may lead to the destruction of at least organic nitrification inhibitors and the subsequent aerobic step shows no further disturbance.

CONCLUSIONS

The efficiency of the biological pre-treatment of the separated streams of tannery wastewater BH and TY depends mainly on the quality of the raw wastewater. Although in some phases COD and DOC-removal was sufficient for meeting the limits of direct discharge, especially in the case of tan-yard wastewater treatment some troubles occurred, which can most likely be ascribed to the tremendous fluctuations of the influent qualities.

It could be shown, that the integration of an oxidation step was successful in order to break up refractory organic compounds, e.g. the oxidative destruction of dyes, and that subsequent aerobic treatment allowed further biodegradation of the oxidation products, resulting in high total degrees of COD and DOC-removal of up to 95% and 91% (referred to the raw TY wastewater), respectively. This effect was found to be optimal in the range of C_{spec} = 1 to 3 g O_3/g DOC_0, for both BH- and TY-wastewater, because further oxidation would lead to the destruction of already biodegradable organic compounds.

Moreover, the remaining contents of ammonia in the aerobic effluents of TY-wastewater of up to 250 ppm could completely be removed by the full nitrification process in the second aerobic step. The identical phenomenon was observed during investigations on BH-wastewater. Nevertheless, it is not yet clear, if the installation of a nitrification step after aerobic removal of the high organic load might have an analogous effect and further investigations on this subject are surely needed.

Compared to conventional treatment of tannery wastewater, the described multiple step treatment for separated streams of tannery wastewater is certainly a high tech process, but under optimized conditions it works probably better and allows the direct discharge of the effluent.

INDICES, ABBREVIATIONS

α:	degree of removal	*sum*:	value summarizing bio and oxi
bio:	value after biodegradation	t_R:	hydraulic retention time
oxi:	value after chemical oxidation		

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