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PARTIAL OXIDATION EFFECTS DURING THE COMBINED OXIDATIVE AND BIOLOGICAL TREATMENT OF SEPARATED STREAMS OF TANNERY WASTEWATER

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ABSTRACT

The ozonation of biologically pre-treated tannery wastewater and the influence of the applied specific ozone consumption onto a subsequent biological treatment were investigated. Combining sum parameters, such as COD, DOC and UV-absorbance, it could be differentiated between mineralization and partial oxidation effects. In the case of UV-removal the newly developed partial oxidation parameters correlate with the subsequent biological removal. It could be shown that partial oxidation of COD is favourable for subsequent biodegradation, whereas further mineralization reduces the effectivity of biological oxidation. The optimal range of subsequent biological treatment was observed at a specific ozone consumption of 1 to 3 g O_3/g DOC_0. As far as the distribution of molecular weight fractions is concerned, the ozonation leads to a relative increase of the low molecular weight DOC-fraction (< 1,000 u), which includes the majority of the residual UV-absorbance at 254 nm. Acute toxicity, measured as luminescence inhibition of *Vibrio fischeri*, is affected by ozonation as well. The calculated $1/EC_{20}$ data decrease with increasing specific ozone consumption. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Biodegradability; molecular weight fractions; ozonation; oxidation products; oxidative wastewater treatment; partial oxidation effects; refractory organic matter; specific ozone consumption; tannery wastewater; toxicity.

INTRODUCTION

Tannery wastewaters 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 sulphate.

The biological treatment of tannery wastewater from a German tannery (full stream wastewater of all process steps) was 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 were not acceptable for direct discharge into rivers (Genschow and Hegemann, 1993). Moreover, during the tanning process some chemicals are applied like fungicides (e.g. benzothiazole), vegetable and synthetic tanning agents (e.g.

sulfonated phenolic polymers) and dyes, which may inhibit the nitrification process or pass through biological steps because of their refractory properties (Reemtsma, 1994; Reemtsma and Jekel 1997).

Thus, we tried to optimise the biological pretreatment by dividing the wastewater of all process steps into two substreams. The pretanning process steps 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). 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 1. Most parameters show remarkable fluctuations and nitrification is often disturbed.

In recent years, the application of oxidation technologies has become more and more interesting for the treatment of poorly biodegradable industrial wastewater, too (Janssens et al. 1984; Langlais et al. 1989; Robson and Rice, 1991; Zimmermann and Richard 1990).

Table 1. Relevant parameters of raw tannery substreams Beamhouse, BH and Tan-yard wastewater,TY and the corresponding effluents of the biological steps (an: anaerobic, ae: aerobic)

Parameter	unit	Beamhouse Waste Water	BH: Aerobic Effluent	Cr-containg. Waste Water	TY: Aerobic Effluent
COD	mg/l	3,500 - 5,000	300 - 500	1,500 - 15,000	150 - 1,100
DOC	mg/l	1,000 - 1,500	80 - 150	600 - 4,500	100 - 300
NH4-N	mg/l	350 - 490	0 - 500	10 - 150	0 - 150
SO4	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
Cl	mg/l	1,000 - 5,000	1,000 - 5,000	600 - 8,000	600 - 8,000
pH		12	7.5 - 8	3	7.5 - 8
resid. time	d		an: 2 ae: 2 - 4		an: - ae: 2 - 4

Table 2. Alterations due to chemical oxidation and possible effects on biodegradability

Changes on	Effect on biodegradability
a) Chemical structure	
Decrease of aromaticity (cleavage of aromatic bounds)	+ enzyme activity
Destruction of high molecular structures (e.g. sulphonated phenolic polymers)	+ destruction of complex steric structures ease cellular transport mechanisms (?)
Incorporation of oxygen	
⇒ Formation of functional groups (hydroxyl, carboxyl, aldehyde etc.)	+ enzyme activity, especially constitutive enzymes
⇒ Increase of polarity	transport mechanisms, uptake
⇒ Decrease of COD / DOC - ratio	+/- less energy output
b) Qualitative properties	
Destruction of toxic substances	+ enzyme activity
Formation of toxic metabolites	-- inhibition of biochemical processes
Destruction of organic nitrification inhibitors	+ nitrification process

Therefore, in order to allow a significantly higher biodegradability of the aerobic effluent and to break up refractory or toxic organic matter and possible nitrification inhibitors, the integration of an oxidation process step seemed to be promising. It was frequently shown, that oxidative treatment improves the biodegradability of poorly degradable organic substrates (e.g. Gilbert, 1982 and 1987; Narkis et al. 1984), and this effect has to be ascribed to alteration of their molecular structure (Table 2). However, little is known about the exact mechanisms taking place during the oxidation of complex organic matrices. In the case of

industrial wastewater, consisting of various unknown compounds, sum parameters, such as COD, DOC and UV-absorbance, might be appropriate to describe the effects of oxidative processes. They might further allow to distinguish between the effects of mineralization and partial oxidation.

Hence, this paper presents the experiences in oxidation of biologically pre-treated separated streams of tannery wastewater with subsequent aerobic biodegradation of the formed oxidation products.

EXPERIMENTALS

All experimental runs with anaerobic/aerobic pre-treated separated streams of tannery wastewater, BH and TY, were carried out in a semi-continuous CSTR (continuously stirred tank reactor) made of glass (height and diameter 20 cm) with a total volume of 6 litre. A bypass of 18 l/h was installed to allow simultaneous measurement of the ozone concentration in the liquid phase using an electro-chemical ozone sensor (ROS, Orbisphere, Neuchatel, Switzerland). The volumetric mass transfer coefficient k_La was determined to 0.38 and 0.73 per minute for ozone and oxygen, respectively (stirrer: 1,500 rpm).

The ozone gas concentrations in the inlet and outlet of the reactor were measured simultaneously using UV-spectrophotometers (BMT 961, BMT, Berlin, FRG). Ozone was produced from technical oxygen (ozone generator Fischer 500, Fischer, Meckenheim, FRG). During all experimental runs a gas flow of 45 litre oxygen per hour and an ozone dose rate of about 5 mg ozone per litre and minute were applied (equivalent to an ozone partial pressure of 1,800-1,900 Pa). The pH-value was adjusted during all tests by adding 0.5 M NaOH via an automatic pH-value control apparatus. Temperature was kept constant at T = 20°C by using a thermostat. A computer-aided on-line ozone mass balance allowed the immediate calculation of the applied ozone dose (input - output) and, taking into account the concentration of ozone in the fluid, also of the real ozone consumption.

Subsequent aerobic biodegradation was determined according to EN 29888 on estimation of ultimate biodegradability (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.

All samples were filtered through a 0.45 µm membrane prior to analysis. For the elimination of possibly formed hydrogen peroxide, a diluted solution of catalase (COD = 30 mg/l) was added before determining the COD-concentration 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). Slight changes of the initial DOC-content of the wastewater may be explained by storage conditions (10°C, darkness). 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 67mM phosphate buffer. Ultrafiltration tests were performed with 200 ml-stir-systems (Amicon, Danvers MA, USA) and membranes with nominal pore sizes of 1,000, 3,000 and 10,000 u. DOC and UV-data of the fractions were determined by the permeate-difference method. Tests on toxicity were carried out in an automated and miniaturized luminescence inhibition test in analogy to DIN 38412 L 34 (inocculum: *Vibrio fischeri* = *Photobacterium phosphoreum*, for details see: Reinke, 1995).

RESULTS AND DISCUSSION

Oxidation of biologically pre-treated separated streams of tannery wastewater

The combined oxidation and subsequent biodegradation make it necessary to set the optimal point of oxidative treatment. Oxidative destruction of the organic matter as indicated by COD and UV-removal, is less favourable in the case of further oxidative mineralization of already biodegradable compounds.

The specific ozone consumption (C_{spec}, unit: g O_3 per g of initial DOC_0) allows to compare the effectivit of oxidative treatment of different types of tannery wastewater. The employment of C_{spec} made it possible t describe the achieved oxidation effects dimensionless with respect to the duration of oxidation. A combine balance of DOC, COD and UV-concentrations at different times allows to differentiate between th oxidation effects of *mineralization* (total oxidation) and *partial oxidation*, which leads to a structural chang of the organic matter by incorporated oxygen (see Table 2). The calculation for COD-reduction throug partial oxidation is done by comparing the averaged degree of oxidation (= COD/DOC-ratio) at differen times (or values of C_{spec}) and is given by the following equation 1:

$$COD_{partoxi} = \left(\frac{COD_0}{DOC_0} - \frac{COD_t}{DOC_t}\right) \times DOC_t \qquad (1)$$

$$\alpha_{CODpartoxi} = 1 - \frac{COD_{partoxi}}{COD_0} \qquad (2$$

Referred to the initial COD content, the degree of COD-removal through partial oxidation can be defined a given in equation 2. The *degree of effectivity* of partial oxidation, $\mu_{CODpartoxi}$, represents the relationshi between partial and total oxidation (Equ. 3). The partial oxidation of UV-active organic constituents i calculated analogously. In order to compare the effectivity of oxidative and biological DOC-removal, we took the difference of the biodegraded DOC and the DOC-content after oxidation related to DOC_0 (Equ. 4).

$$\mu_{CODpartoxi} = \frac{COD_{partoxi}}{COD_0 - COD_t} \qquad (3)$$

$$\alpha_{DOCbio} = \frac{DOC_{oxi} - DOC_{bio}}{DOC_0} \qquad (4$$

Oxidation and subsequent biodegradation of Beamhouse wastewater

Figure 1 shows the degree of oxidative removal COD, DOC and UV after ozonation and the $_{DOCsum}$ summarizing oxidative and subsequent biological DOC-removal. As expected, all parameters increase with elevated values of C_{spec}, 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 50%. 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.

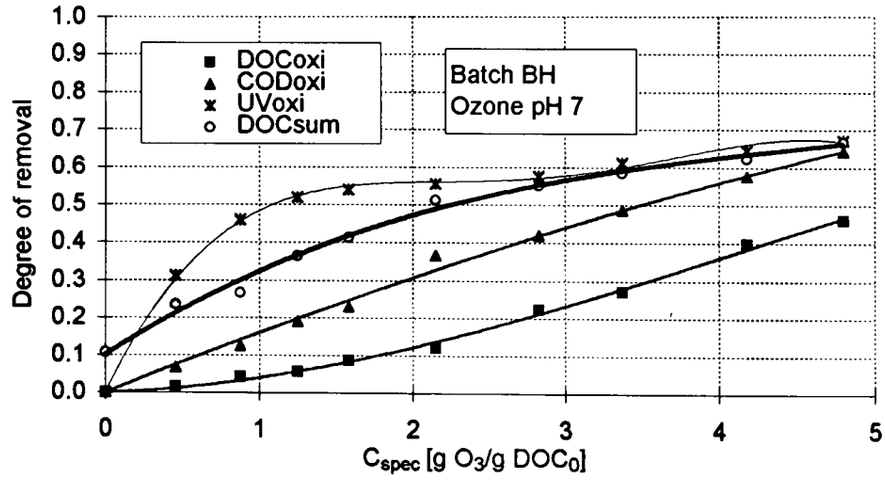

Figure 1. Oxidative removal of COD, DOC, UV and α_{DOCsum} of BH vs. C_{spec} (BH: COD_0 = 108 mg/l, DOC_0 = 60 mg/l, UV_0 = 72.8 m^{-1}).

Therefore, COD/DOC and UV/DOC-ratios are shifted from 1.8 to 1.2 and from 1.2 to 0.7, respectively, a C_{spec} = 4.8 g/g. Figure 2 illustrates the DOC-removal by subsequent biological treatment of the ozonate samples.

Whereas on one hand the oxidative DOC-destruction increases with an increasing specific ozone consumption. (up to 50% DOC-removal at C_{spec} = 4.8 g/g, Fig. 1), the subsequent biological degradation is most efficient at a specific ozone consumption of 1.5 to 3 g/g. Further oxidation clearly diminishes the degree of biological DOC-removal, as explained above. The partial oxidation of UV gains its optimum a little bit earlier but generally coincides with this effect. As long as the partial oxidation of COD dominates the COD-mineralization (for $_{CODpartoxi} > 0.5$), biological DOC-removal is supported as well. However, the curve of $_{CODpartoxi}$ amounts up to C_{spec} = 2 g/g and remains at a level of 0.2. The averaged ozone consumption per g of reduced COD was calculated to 3.2 - 5.1 g O_3/g COD for BH wastewater. During investigations on another batch of Beamhouse wastewater (COD_0 = 105 mg/l, DOC_0 = 46.2 mg/l, UV_0 = 70.8 m^{-1}), we found a similar maximum range of α_{DOCbio} and a decrease of $\alpha_{UVpartoxi}$ and α_{DOCbio} above C_{spec} of 3 g/g.

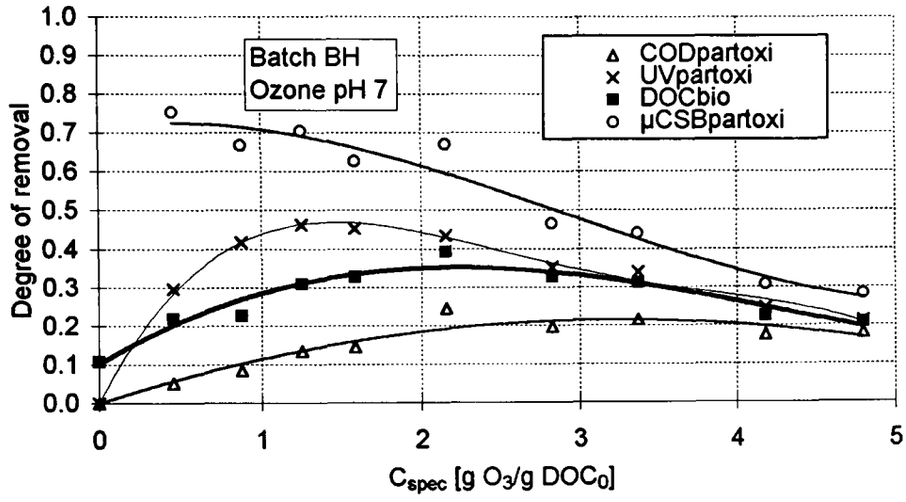

Figure 2. Degree of biological DOC-removal and partial oxidation parameters of BH-wastewater versus C_{spec}

Oxidation and subsequent biodegradation of Tan-yard wastewater

Generally, the application of ozone on Tan-yard wastewater leads to similar effects on α_{CODoxi}, α_{DOCoxi} and α_{UVoxi} (Figure 3). Subsequent biodegradation (Figure 4) is favourable at a range of C_{spec} = 1 to 3.5 g/g.

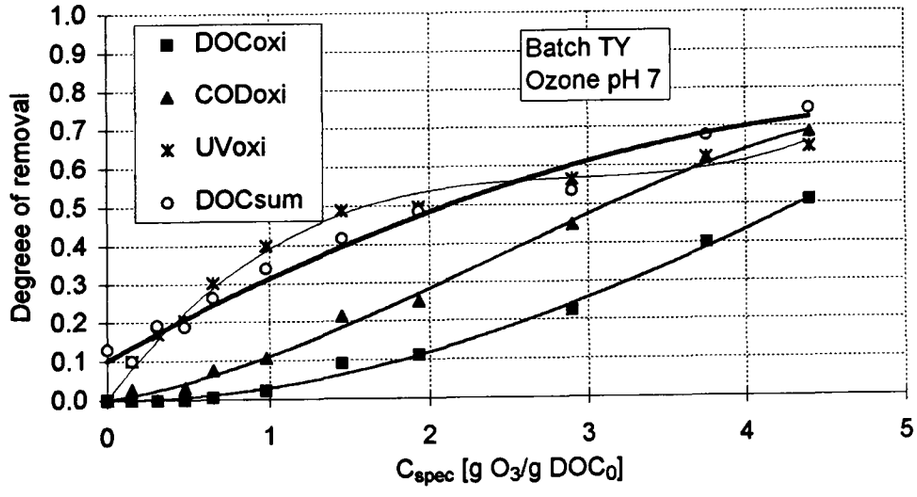

Figure 3. Oxidative removal of COD, DOC, UV and α_{DOCsum} of TY versus C_{spec} (TY: COD_0 = 450 mg/l, DOC_0 = 185 mg/l, UV_0 = 258 m^{-1}).

As in the case of BH, the data of $\alpha_{UVpartoxi}$ are in good agreement with this finding, while the $\alpha_{CODpartoxi}$ still increases up to C_{spec} = 3 g/g. Again it becomes obvious, that for $\mu_{CODpartoxi}$ > 0.5 biological DOC-removal is not affected in a negative way.

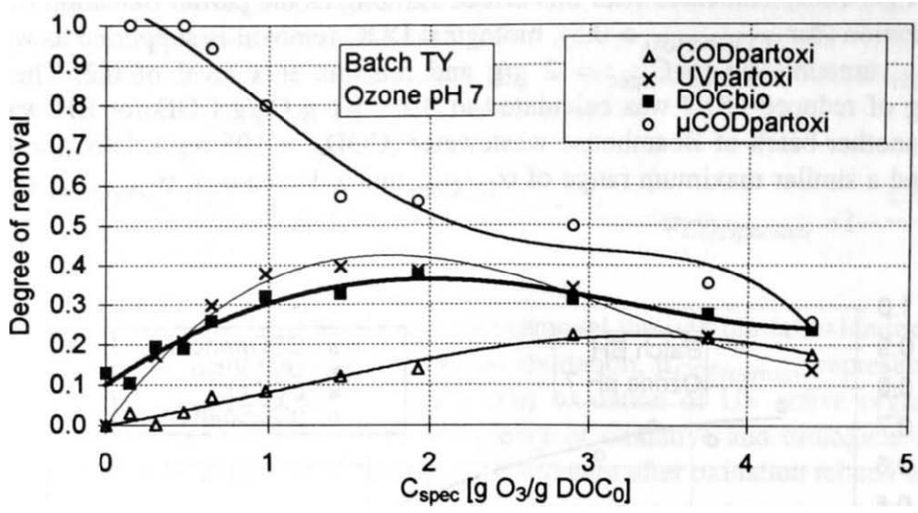

Figure 4. Degree of biological DOC-removal and partial oxidation parameters of TY-wastewater versus C_{spec}.

The COD/DOC and UV/DOC-ratios are diminished from the beginning to C_{spec} = 4.4 g/g from 2.4 to 1.5 and from 1.4 to 0.9, respectively. The averaged ozone consumption per g of reduced COD was calculated to 1.8 - 4.2 g O_3/g.

In studies on a second batch of Tan-yard wastewater (COD_0 = 130 mg/l, DOC_0 = 54.2 mg/l, UV_0 = 70.5 m^{-1}), the optimal $_{DOCbio}$ was determined to 0.35 - 0.4 at a wide range of C_{spec} of 1.0 to 4.5 g/g.

Changes in the distribution of molecular weight fractions

Figure 5 shows the results of ultrafiltration tests performed with ozonated BH wastewater. In general, the residual DOC decreases with elevated values of C_{spec}. The biologically pre-treated BH contains the different molar mass fractions in nearly equal percentages (high: >10,000 u; low molecular weight: < 1,000 u). During ozonation a fragmentation of high molecular weight substances can be observed: at C_{spec} = 2.5 g/g already 78 % of the DOC are of low molecular weight.

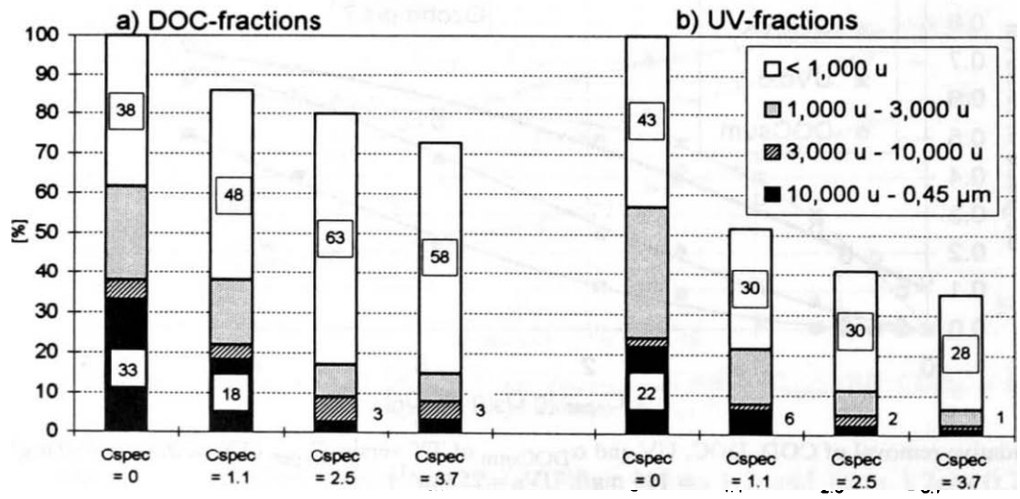

Figure 5. Changes of the molecular weight distribution of BH wastewater by ozonation at elevated values of C_{spec}. a) DOC-fractions: DOC_0 = 64 ppm; b) UV-fractions: UV_0 = 76.5 m^{-1}.

Further oxidation does not lead to any significant changes in the molecular weight distribution, but to an increasing mineralization, especially of low molecular weight substances.

The calculated data of the UV-fractions are given in Figure 5 b. At C_{spec} = 1 g/g the UV is reduced to almost 50%, at C_{spec} = 3.7 a further removal of only 14% is observed.

Although at C_{spec} of 1.1 g/g a UV-removal of all fractions can be stated, the relative percentages of the low molecular weight fraction rises from 43 rel.% to 78 rel.% at C_{spec} = 3.8 g/g. Moreover, the oxidation causes a significant decrease of the UV to DOC-ratio of 1.34 to 0.59 for the low and of 0.79 to 0.46 of the high molecular weight fraction, respectively.

The ultrafiltration of oxidized TY-wastewater shows a similar pattern of the DOC and UV-distribution (Figure 6 a and b). At C_{spec} = 3.8 g/g the DOC-fraction of low molecular weight substances is 62 rel%, referred to the actual DOC-content, in contrast to 42 % of the original sample. The fraction of the high molar masses decreases from 32 rel% to 16 rel% (absolute values: 57 ppm to 19.4 ppm DOC).

The distribution of UV-absorbance changes rapidly during ozonation. After applying 1.1 g ozone per g of initial DOC almost 50% removal is obtained and again especially the low molecular weight fraction increases from 26 rel% to 59 rel% (absolute data: 26 to 15.5 m^{-1}). The UV/DOC-ratios are decreasing from 2.1 to 0.6 and from 1.1 to 0.6 l mg^{-1} m^{-1} for the high and low molecular mass fraction, referred to C_{spec} = 0 and 3.8 g/g, respectively.

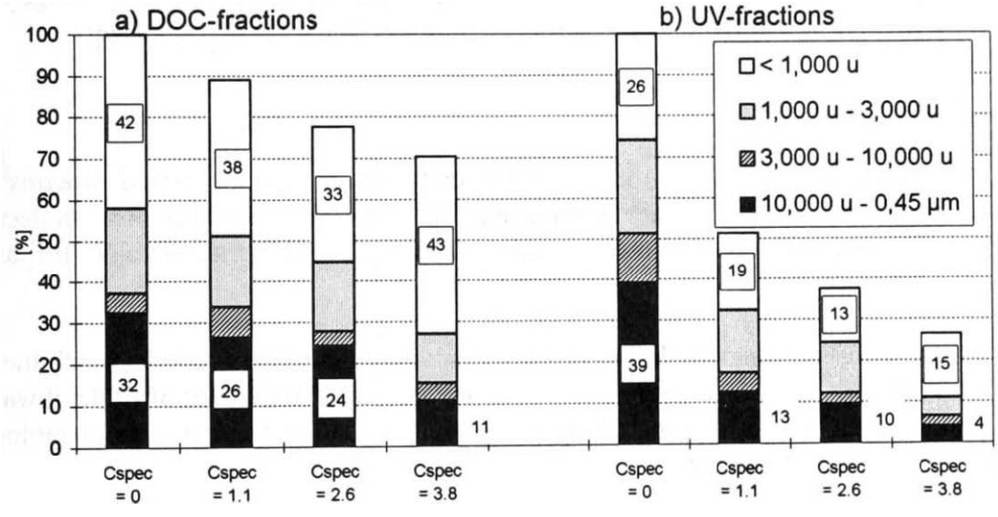

Figure 6. Changes of the molecular weight distribution of TY wastewater by ozonation at elevated values of C_{spec}. a) DOC-fractions: DOC_0 = 176 ppm b) UV-fractions: UV_0 = 275 m^{-1}.

The estimated value of UV/DOC of 4.5 l mg^{-1} m^{-1} for the fraction of 3,000-10,000 u is likely due to the presence of non-biodegradable vegetable or synthetic tanning agents (e.g. chestnut-extract or sulphonated phenolic polymers), which show values in the same range.
Summarizing the oxidation effects on the distribution of DOC and UV-fractions of BH and TY wastewater, the ozonation leads to a fragmentation of high molecular weight substances and produces molecules of low molar masses which include the majority of the residual UV-absorbance.

Changes in acute aquatic toxicity (luminescence inhibition of Vibrio fischeri)

The determination of luminescence inhibition was performed with non-concentrated original samples. Due to the very low initial level of 47% and 40% luminescence inhibition for BH and TY, rsp., using the lowest possible dilution of 1 to 2 (see experimental section), it was not possible to calculate EC_{50} data. Thus, the level of 20% effective concentration was chosen to characterize oxidation effects.

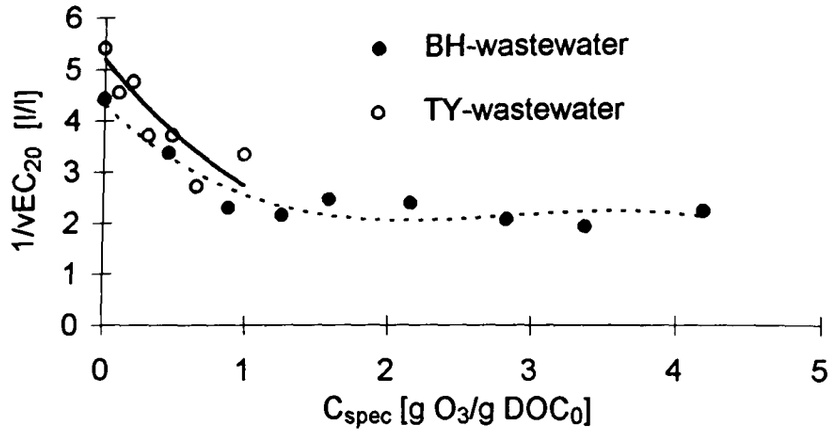

Figure 7. Calculated $1/vEC_{20}$-data of BH and TY-wastewater versus C_{spec} (= dilution factor: ml final volume per ml of sample).

The reciprocal $1/vEC_{20}$ data are given in Figure 7 (= necessary dilution, unit: final volume in ml per ml of sample volume). As far as TY wastewater is concerned, it was not always possible to determine or extrapolate $1/vEC_{20}$ data, because of very low values below 15%. For both substreams of tannery wastewater examined, the ozonation procedure affects the acute toxicity in a significant positive way. Referring the $1/vEC_{20}$ data to the actual corresponding DOC-content leads to the so-called $1/dEC_{20}$ values, which show the same tendency as observed in Figure 7. The $1/dEC_{20}$ values lay in the range of 3.4 to 4 x 10^{-2} and 2.5 to 3.5 x 10^{-2} l mg^{-1} for BH and TY wastewater, respectively (at $C_{spec} > 1$ g/g).

CONCLUSIONS

The application of ozone for the oxidation of biologically pre-treated separated streams of tannery wastewater is effective and allows further biodegradation. The shift towards low molecular weight compounds and the significant lowering of the acute toxicity could be favourable for an enhanced biodegradability.

In the case of UV-absorbance, the newly defined partial oxidation parameters correlate with the subsequent biological removal. Although, this correlation is less clear for the partial oxidation of COD, it was found that as long as the removal of COD is dominated by the partial oxidation the subsequent biological DOC-removal is not affected in a negative way.

The relatively high amount of non-degraded high molecular constituents in the BH-wastewater after biological pretreatment might be ascribed to biogenic organic matter of the raw hides, like hydrolyzable complex proteins and fats. Moreover, detailed information about persistent substances applied in the process steps of the Beamhouse wastewater are not yet available. Reemtsma et al. (1993) showed the persistence of high molecular and UV-active vegetable and synthetic tanning agents, which are applied in the process steps belonging to the Tan-yard wastewater. These findings could partly confirm the effects observed during TY-wastewater treatment.

Despite a better biodegradability of poorly degradable industrial wastewaters after oxidative treatment in general, partial oxidation parameters may provide valuable additional information and should be considered as well. The optimal conditions for operating a combined biological and oxidative treatment of industrial wastewater may surely depend on the wastewater characteristics and have to be evaluated individually.

INDICES

oxi, bio: value after chemical oxidation and biodegradation
UV: UV-absorbance at 254 nm
partoxi: value due to partial oxidation
sum: value summarizing bio and oxi

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