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Abstract: Conventional biological wastewater treatment processes often fail in the elimination of finishing agents contained in textile wastewater such as dyes, surfactants, and softeners. Therefore, discharges from the textile industry are known as a major source of water pollution reaching groundwater and even drinking water treatment. Physicochemical treatment and advanced treatment processes (AOP) were applied to eliminate the pollutants prior to discharge. Ozone (O_3), O_3/UV, hydrogen peroxide/UV (H_2O_2/UV), Fenton's reagent (Fe^{2+}/H_2O_2) were applied to eliminate by oxidation while ultrasonication (US) alone, US/UV or powdered activated carbon (PAC) were used for the physicochemical treatment. Elimination was monitored by a conventional sum parameter analyses (COD, BOD, DOC) while gas chromatography/mass spectrometry (GC/MS) and liquid chromatography coupled with MS and tandem mass spectrometry (LC/MS and -MS/MS) was applied for follow-up of pollutants and their degradation products. The application of PAC, Fenton, and O_3/UV resulted in the highest dissolved organic carbon elimination. A complete or partial elimination and/or degradation of non-polar or polar pollutants was observed by GC/MS or flow injection analysis/MS (FIA/MS) respectively. LC/MS and MS/MS analyses confirmed that ethoxylated surfactants (AEO) present

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in the original wastewater could be oxidized or destroyed resulting in carboxylated AEO and polyethylene glycol (PEG) or even carboxylated PEG.

Keywords: Advanced oxidation process (AOP), elimination monitoring, gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS), textile wastewater

INTRODUCTION

The textile industry represents an important economic sector in many countries, but in parallel generates large amounts of heavily polluted wastewater containing predominantly a wide range of unpolar as well as polar organic substances. The compounds found in this wastewater are monomers, oligomers, and polymers. The spectrum is composed of substances which had been used before as auxiliary products in textile production and treatment, were washed out of the textile, and had run off with the waste water.

The majority of pollutants in textile wastewater are non-biodegradable and/or non-removable by biological waste water treatment. Therefore, these organic compounds resist conventional chemical and advanced biological wastewater treatment processes like biological membrane treatment (MBR). Moreover, some of these organic pollutants develop toxic effects to the biocoenosis applied in wastewater treatment processes. For this reason, other methods are being studied as alternatives to biological and conventional physicochemical processes.

Advanced oxidation processes (AOPs) which generate extremely reactive and non-selective hydroxyl radicals ($^{\bullet}OH$), therefore, should be applied as pre-treatment steps for the disintegration and oxidation of refractory and hazardous pollutants in textile wastewater. Ozone (O_3) and hydrogen peroxide (H_2O_2) alone or in combination with catalysts (Fe^{2+}) optional supported in activity by high-energy radiation, e.g., UV light will be applied which has recently proved under non-substance or substance specific analysis to be a potential highly efficient technique for wastewater (1–6) and drinking water (7) treatment.

The different AOP reacting systems are characterized by the production of $^{\bullet}OH$ radicals. For the most applied AOP techniques, O_3/H_2O_2, H_2O_2/UV, O_3/UV, and Fenton, the pH of the solution influences the rate of radical generation for the system. In addition it is important to consider that during photooxidation processes the pH of the reaction medium decreases due to the formation of acidic species. For highest efficiency of pollutant abatement therefore it is necessary to adjust the pH of the water to be treated according to the treatment technique (4, 6). During our experiments pH was not modified because physicological conditions adjusted in the effluent of the textile wastewater mixing basin should allow a following biological treatment step without any additional pH adjustment.

The effect of advanced treatment processes as a pre-treatment step for the elimination of organic load or improving the biodegradability of textile wastewater by primary degradation was examined by sum parameter analyses like COD (chemical oxygen demand), DOC (dissolved organic carbon content) or BOD (biochemical oxygen demand). The color removal was monitored recording UV/VIS-spectra. The fate of the pollutants first should be followed-up in textile wastewater by substance specific wastewater analyses to recognize the substance specifically degradation of wastewater pollutants and the generation of oxidation products as already performed in the treatment of drinking water (7) and wastewater (5), in particular with tannery wastewater (1–3). Therefore gas chromatography-mass spectrometry (GC-MS) in positive electron ionisation (EI(+)) mode and atmospheric pressure ionization (API) in combination with flow injection analysis (FIA) or liquid chromatography-mass spectrometry (LC-MS) and tandem mass spectrometry (MS-MS) were applied to elucidate the degradation and the whereabouts of the pollutants during physicochemical and AOP treatment.

METHODS

Materials

The wastewater from the textile industry was a representative mixture of effluents from different finishing processes taken from mixing basin prior to discharge into the municipal sewerage of the city of Aachen (Germany). The wastewater was filtered by glass fiber filter removing particles >1 μm prior to treatment and was kept at -18°C for preservation.

Chemicals and gases used in the study were already described by Schrank et al. (4). Powdered activated carbon (PAC) with a surface area of 1200 m^2 g^{-1} and a particle size of 7 μm (Norit SA UF) was a gift of Norit Deutschland GmbH (Düsseldorf, Germany).

Physicochemical and Chemical Wastewater Treatment Procedures

Ozone (O_3) and O_3/UV treatment were performed applying ozone dosage periods of 10, 20, and 30 minutes for the treatment of 500 mL of the wastewater without or in combination with an UV radiation. The reactions with the exception of the Fenton process were performed at the original pH of the textile wastewater (cf. Table 1) using a three-necked reactor made from glass (Pyrex) with a capacity of 2000 mL. The reaction was performed using a 15 W medium pressure mercury lamp as UV source (Heraeus, Germany), which was surrounded by a quartz thimble. The reactor and the quartz thimble were doublewalled and water was used in a cooling circuit

Table 1. Results of conventional chemical analyses before and after the application of different physicochemical and chemical treatment procedures

Treatment	No treatment	O_3	PAC	O_3/UV	US/UV	US	H_2O_2/UV	Fenton
Treatment period [min]	0	30	120	30	30/30	30	120	120
COD [mg/L]	1045	834	776	750	946	1000	893	793
BOD_5 [mg/L]	272	315	210	317	277	274	310	257
DOC [mg/L]	330	300	260	280	290	300	300	270
NH_4^+-N [mg/L]	14.7	9.2	14.0	11.46	14.3	14.0	—	—
NO_3^--N [mg/L]	0.20	1.1	0.22	1.60	0.53	0.51	—	—
o-PO_4^{3-}-P [mg/L]	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0
P_{total} [mg/L]	3.1	2.9	2.8	3.0	3.1	3.1	2.9	<1,0
SO_4^{2-} [mg/L]	512	525	499	515	510	514	519	—
$pH_{(t=0)}$	8.3	8.3	8.3	8.3	8.3	8.3	8.3	3.0

to maintain a constant temperature of 28°C as described in detail by Schrank et al. (2–4).

The Fenton reactions were carried out over a period of 2 h in the Pyrex tube (4) as described before. The initial pH was adjusted at 3 and concentrations of 150 mg L^{-1} of $FeSO_4 \times 7H_2O$ and 400 mg L^{-1} H_2O_2.

The experiments applying H_2O_2/UV were performed at the original pH of the textile wastewater (cf. Table 1) and under the conditions as described by Schrank et al. (4). During reaction the mixture inside the reactor was continuously stirred using a magnetic stirrer and a Teflon-coated magnetic stirring bar.

The activated carbon treatment was carried out in the reactor also used for AOP treatment. 250 mg L^{-1} of PAC (Norit SA UF) first were added to the vigorously stirred wastewater while the mixture was continuously stirred over a period of 2 h. After settling, samples were taken from the supernatant.

Ultrasonification (US) and US/UV treatment were performed by means of an ultrasonic transducer (20 kHz) (B. Braun, Germany) applying a power of 200 Watts. It was placed in a glass beaker of 600 mL capacity. The US impulse then was transmitted into the wastewater. The sample (500 mL) was treated for a period of 30 minutes using US. In parallel, UV and US were used for treatment for a period of 60 minutes intercalating them by 5 minutes. The same procedure was used while in parallel UV-radiation was applied to the reaction mixture using the UV-lamp described before.

Conventional and Substance Specific Chemical Analyses

Parameters of conventional chemical analyses performed are enlisted in Table 1. Standard methods were performed of all chemical analyses as described in the German Standard Methods for the Examination of Water, Waste Water and Sludge (8). The Chemical Oxygen Demand (COD) was determined using colorimetric methods. The Total Organic Carbon content was determined as Dissolved Organic Carbon (DOC) and was analyzed by a DIMATOC 2000, (DIMATEC, Essen, Germany). UV/VIS-spectra of the wastewater samples were recorded between 200 and 800 nm applying a layer thickness of 1 cm using a Beckmann DU-60 UV/VIS spectrometer with a scan speed of 750 nm min^{-1}.

The samples for substance specific chemical analyses, which were obtained after different physicochemical or chemical processes were first concentrated by solid phase extraction (SPE) using commercially available C_{18}-SPE cartridges filled with C_{18} material (9). Prior to concentration step SPE cartridges were conditioned sequentially by 6 mL of acetone, methanol, and ultra-pure water prior to extracting the non-polar and polar pollutants. With this material the very strong polar compounds, however, were not adsorbed. For GC-MS analysis hexane and for FIA-and LC-MS and -MS-MS analyses methanol were used for the desorption of pollutants from SPE cartridges. Three bed volumes of solvent were applied. The eluates obtained were reduced to a fixed volume in a gentle stream of N_2. The eluate then could be used for chromatography and mass spectrometric analyses.

For GC-MS-analyses a Hewlett Packard HP 6890 GC system in combination with a CTC A 200 S autosampler adapted to a Finnigan MAT 95 XL mass spectrometer was used for analyses. Extracts were separated on a fused-silica capillary column (Varian vf 5 ms, 30 m × 0.25 mm I.D., film thickness 0.1 μm). The conditions were as follows: carrier gas, helium, linear gas velocity, 15 cm s^{-1}; injector temperature, 280°C; transfer line temperature, 280°C; temperature program applied: 60°C (3 min); 10°C/min auf 280°C (15 min).

Positive electron impact (EI+) ionization was performed with an ionization energy of 70 eV. The resolution was 1000 mmu recording masses from 50–450 m/z in full scan mode. The electron multiplier was operated at 1400 V. The temperature in the ion source was 240°C (4).

For mass spectrometric analyses of polar compounds flow injection analysis coupled with mass spectrometric detection (FIA-MS) and liquid chromatographic-mass (LC-MS) and -tandem mass spectrometric detection (LC-MS-MS) were applied. For coupling APCI or ESI interfaces, both from Finnigan (San Jose, USA), were applied as described by Schrank et al. (2–4). The flow split ratio was adjusted to 1:2 in favor of the MS in ESI mode compared to waste. The exception that the electron multiplier voltage was adjusted to 1700 V in the MS mode and 2000 V in the MS/MS mode with a conversion dynode voltage at 15 kV. LC separations prior to the MS-, MS-MS- and UV detection were carried out on a Multospher 100 RP 18 column (C_{18}, 5 μm, spherical; 250 × 4.6 mm I.D.) from the CS Chromatographie Service (Langerwehe, Germany). Applying LC-MS or MS-MS, 10 μL of standard solutions or SP extracts were injected onto the column. The gradient for separation applying methanol/acetonitrile 50:50 (A) in combination with Milli-Q-purified water (B), both containing 0.1% formic acid, was programmed as follows: Starting with 10% A/90% B the concentration was changed linearly to 90% A/10% B within 12 min. Up to 30 min the composition was kept constant. The overall flow rate was adjusted to 0.8 mL min^{-1} (2–4).

RESULTS AND DISCUSSION

Chemical sum parameter analyses, UV/VIS-absorbance and substance specific chemical analyses for the assessment of untreated textile wastewater and wastewater after various types of physicochemical, chemical and AOP treatment were used to monitor treatment efficiency. A representative sample of textile wastewater taken from the mixing basin after textile processing and prior to discharge into sewerage was used for our elimination and degradation studies. Despite the option to obtain improved treatment results with a preceding pH adjustment treatment was performed with the textile wastewater at its original pH with the exception of the Fenton treatment.

Conventional Chemical Analyses

In Table 1, the results of the analyses for the parameters COD, DOC, BOD_5, nitrogen, phosphorous parameters, and sulphate of the original wastewater and after the application of different treatment techniques to textile wastewater are enlisted. All our treatment steps—physicochemical and AOP—were aimed at the recognition of the elimination or modification of the chemical structures of recalcitrant organic substances, which should be monitored by MS. Because of high energy consumption no mineralization effects were desired. Moreover, an enhancement in biodegradability was expected and desired during O_3 and AOP treatment. The generation of toxic degradation products, however, was not examined because the AOP pre-treated wastewater was designated to a biological treatment prior to discharge. The results of ozonisation without UV radiation and the application of UV radiation in parallel with O_3 treatment are presented together with other AOP methods like H_2O_2/UV and Fenton (Fe^{2+}/H_2O_2) in Table 1. The results of the physicochemical treatment methods ultrasonication (US) without and with UV radiation (US/UV) and adsorption by PAC were also enlisted.

The results of inorganic nitrogen, phosphorous, and sulphur compound analyses in the original textile wastewater showed no exceptional concentrations (cf. Table 1). The sample contained low concentrations of organic and inorganic phosphorous and sulphate. These parameters were not influenced and changed by AOP treatment to a larger extent than in their ranges of analytical variations. The exception was, that under the Fenton treatment also organic phosphorous compounds were eliminated which took place by precipitation after destruction of the organic phosphorous compounds. Nitrogen was determined as ammonium and nitrate nitrogen. As expected, a slight increase was observed for nitrate concentrations under strong oxidation conditions - O_3 or O_3/UV - in combination with an in-parallel decrease of the concentration of reduced nitrogen constituents.

The organic load was monitored by sum parameter analyses of COD, DOC and BOD_5. In our experiments, COD decreased because of a selective or unselective oxidation of pollutants contained in the wastewater while as expected DOC remained constant. Similar behavior was reported by Balakrishnan et al. (10), Iaconi (11), and Schrank (2–4) in the treatment of tannery wastewater. Under these treatment methods in-parallel an improved biodegradability determined by an increasing BOD_5 (20–35 mg O_2 L^{-1}) was observed as also reported (11). Treatment with Fenton's reagent, however, resulted in a decrease of BOD as well as DOC because of an increased elimination of pollutants by adsorption onto the ferric hydroxide which precipitates during Fenton's reaction. The best elimination results for organic pollutants from textile wastewater were observed with the application of powdered activated carbon (PAC) while ultrasonic treatment with and without support of UV radiation (cf. Table 1) failed in the elimination or destruction of compounds.

Analytical results obtained by conventional chemical analysis proved that the aim of treatment, i.e. modification in structures possibly for an improved biodegradability, partly could be reached by the oxidation processes O_3, O_3/UV and H_2O_2/UV. Compounds were oxidized resulting in structural modifications. Bond scission had taken place and new compounds were generated, containing more oxygen atoms which made these compounds more polar resulting in an increase of biodegradability (BOD) and an in-parallel decrease in COD. The application of these methods did not lead to an elimination of carbon, recognizable by DOC determinations. The application of Fenton's reagent and PAC treatment produced ferric hydroxide or activated carbon precipitates, respectively, loaded with adsorbed pollutants while the physicochemical treatment of ultrasonification (US) and US/UV led to marginal changes in COD or DOC.

The comparison of UV/VIS-spectra recorded between 200 and 800 nm proved that the best results in diminishing the dark blue color of the textile wastewater were achieved with the application of O_3 and O_3/UV. The application of AOPs using H_2O_2/UV or Fenton's reagent in decolorization was quite ineffective, whereas O_3 or O_3/UV treatment was quite effective in the destruction of the aromatic or conjugated aliphatic π-electron systems which as chromophoric groups were responsible for the light absorption between 250 and 300 nm. So after O_3 or O_3/UV treatment the color even reduced by H_2O_2/UV or Fenton treatment now disappeared completely (cf. Fig. 1).

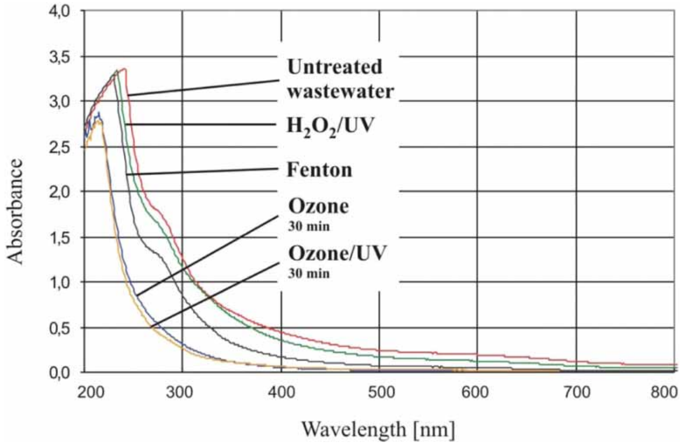

Figure 1. UV/VIS absorbance of untreated and ozone or AOP treated wastewater recorded in the range of 200–800 nm.

Substance Specific Analysis Applying Mass Spectrometry

In parallel to conventional analyses, substance-specific analytical techniques, i.e., mass spectrometric methods (MS) such as GC-MS, FIA- or LC-MS and LC-MS-MS analyses, were performed. With these procedures much more background information about compounds which persist treatment applied and those which could be partly oxidized or even mineralized by the various AOP techniques will become available. Using rough screening methods of pattern recognition prior to the more time-consuming identification of compounds prompt information we expected (12, 13, 16) as to why in contrary to the treatment applied to tannery wastewater (2–4) a moderate improvement in biodegradability here was observed.

Non-Polar Organic Pollutants

In order to monitor the volatile, non-polar pollutants, in a first step we chose the GC-MS screening approach in the positive electron ionisation (EI+) mode. This procedure provided different information:

1. the diagnostic extracted ion current traces for characterization,
2. the EI mass spectra of fragments for identification by library search, and
3. the standardized total ion current traces (TIC) used for screening applying pattern recognition.

We followed up this procedure and tried to characterise the volatile compounds observed in GC-MS TICs after the different treatment steps by means of the diagnostic extracted ion current traces prior to the more extensive EI spectrum library search applied for identification. For a semi-quantitative judgement of elimination efficiencies then TICs which had been recorded after the different treatment steps can be standardized to the TIC of the original untreated wastewater extract (=100%). Then they can visually be compared to recognize the elimination obtained under different treatment processes.

As an example of the procedures performed during the above-mentioned characterization process of volatile organic pollutants and their behavior under different treatment conditions substance-characterising extracted mass traces of the untreated and the O_3/UV treated sample were displayed together with their TICs as shown in Fig. 2. So beside the mass traces of saturated aliphatic hydrocarbons (m/z 57, 71) (cf. Fig. 2a or e), unsaturated aliphatic hydrocarbons (m/z 83) (cf. Fig. 2b or f) and alkylated aromatic hydrocarbons (m/z 91) (cf. Fig. 2c or g) besides the mass traces of the untreated wastewater and the O_3/UV treated sample are plotted together with their TICs (cf. d or h) in Fig. 2. Compared to the untreated wastewater O_3/UV-treatment, as expected, resulted in qualitative as well as quantitative changes of compounds in selected extracted mass traces. It could be recognized from

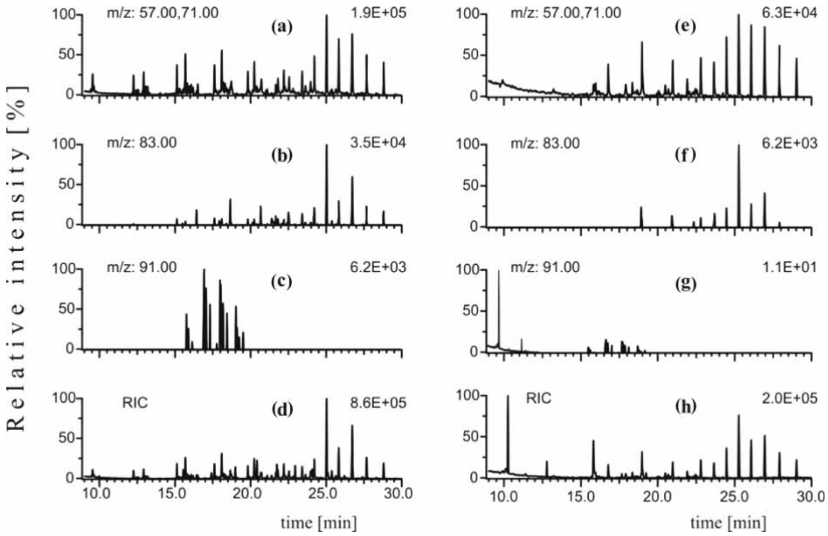

Figure 2. GC-MS total ion current traces of (d) untreated textile wastewater, and (h) after O_3/UV treatment. (a–c) characteristic extracted mass traces of the untreated and (e–g) the O_3/UV treated sample proving (a and e) the presence of saturated aliphatic hydrocarbons (m/z 57, 71), (b and f) unsaturated aliphatic hydrocarbons (m/z 83), and (c and g) alkyl-substituted aromatic hydrocarbons (m/z 91).

decreasing ion current intensities in the selected mass traces (cf. Figs. 2a vs. 2e, 2b vs. 2f etc.) that the saturated aliphatic (m/z 57, 71) as well as the unsaturated aliphatic hydrocarbons (m/z 83) decreased while the mass traces of the aromatic compounds (cf. Fig. 2c vs. 2g; m/z 91) proved the total elimination of volatile aromatic compounds during O_3/UV-treatment.

Qualitative analysis of volatile compounds by NIST library search proved that the compounds present in the untreated wastewater were predominantly saturated aliphatic hydrocarbons, while smaller amounts of unsaturated aliphatic and aromatic hydrocarbons could be observed as also found in the extracted mass traces.

The visual pattern recognition approach in the GC-MS screening (16) applied to all samples under research provided quite a lot of information: comparing GC-MS total ion current intensities of treated samples (Fig. 3b–h) standardized to the TIC of the untreated wastewater in Fig. 3a which defined the 100%-scale, it became obvious that with the application of physicochemical and chemical treatment techniques a decrease in signal height happened which is proportional to changes in concentration. Many peaks observable in the untreated wastewater even have disappeared completely proving a highly efficient elimination while in parallel some peaks appeared in the TICs after O_3 (Fig. 3f) and O_3/UV (Fig. 3g) treatment proving the generation of new compounds. These new compounds were observed in these TICs at shorter

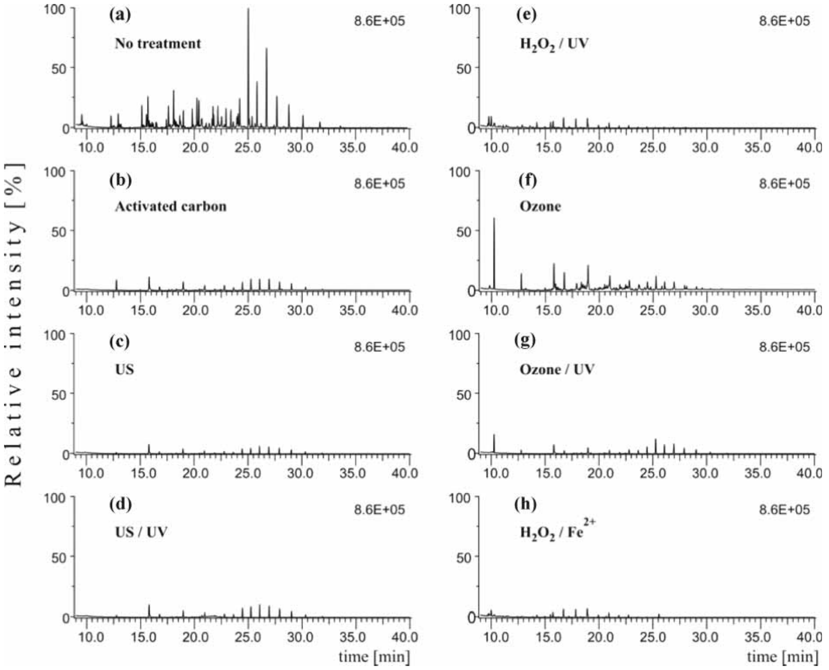

Figure 3. GC-MS total ion current traces (TIC) of C_{18}-SPE for (a) untreated textile wastewater and (b–h) standardized TICs of textile wastewater after (b) activated carbon, (c) US, (d) US/UV, (e) H_2O_2/UV, (f) O_3, (g) O_3/UV and (h) H_2O_2/Fe^{2+} treatment.

retention times (RT) proving that smaller molecules had been generated. By NIST library search compounds were identified as aliphatic alcohols generated from oxidative surfactant degradation.

Polar Organic Pollutants

In a second more time-consuming step, the polar compounds of untreated and treated textile wastewater were determined. Mass spectrometric detection (MS) in combination with atmospheric pressure ionisation (API) techniques such as APCI or ESI first in the FIA-MS mode for screening purposes was performed in the positive and negative mode. In textile wastewater, polar compounds were estimated to be the most important pollutants because the compounds applied in textile finishing processes are predominantly polar and easily water soluble. In addition, polar compounds would be generated by oxidative degradation processes which took place under O_3 or AOP treatment.

Application of the soft ionizing interfaces APCI or ESI for polar compounds in FIA-MS mode resulted in overview spectra which could be used to monitor elimination and/or modification of compounds under different AOP conditions by means of visual pattern recognition. In contrast to the pattern recognition approach applied to non-polar compounds using ion current traces now the overview spectra providing the pattern of pollutant ions together with the molar mass information of these pollutants (9, 13–16). To recognize quantitative changes and judge the elimination efficiencies of the different treatment processes by pattern recognition FIA-MS overview spectra of treated samples (Fig. 4b–h) recorded in the positive mode were standardised to the overview spectrum of the untreated wastewater extract (Fig. 4a). With this approach we observed the compounds in the methanol eluates of the C_{18}-SPE concentrates of

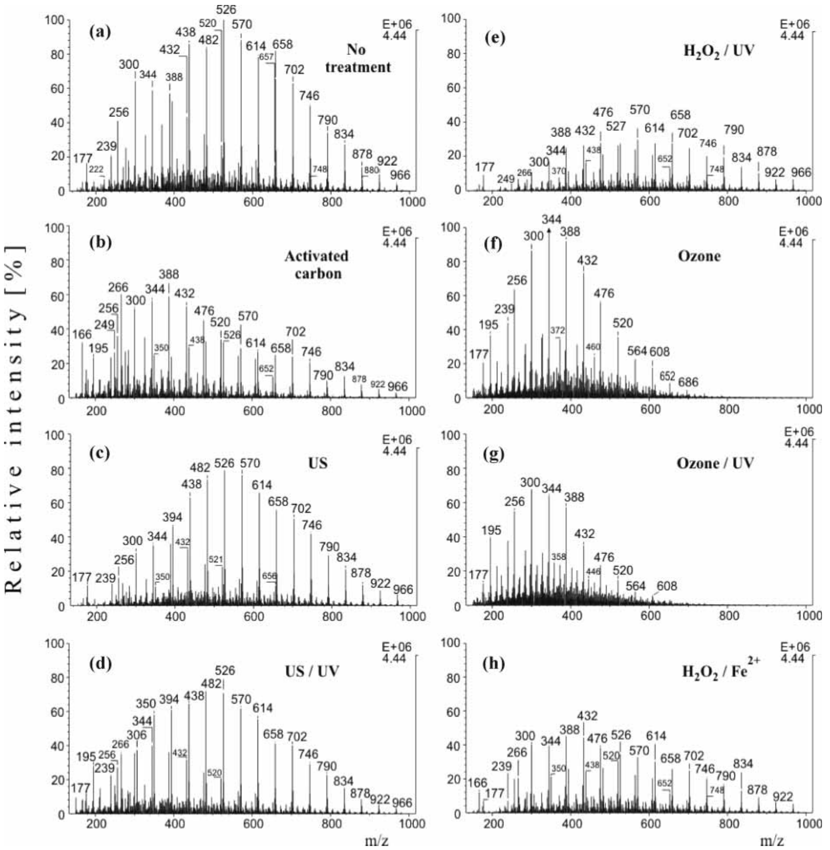

Figure 4. APCI-FIA-MS(+) loop injection spectra, subsequently called “overview spectra” for textile wastewater of C_{18}-SPE extract (a) without treatment. (b–h) overview spectra of textile wastewater after (b) activated carbon, (c) US, (d) US/UV, (e) H_2O_2/UV, (f) O_3, (g) O_3/UV and (h) H_2O_2/Fe^{2+} treatment, all standardised to concentration and dilution factor of untreated sample in (a).

untreated and treated wastewater. So qualitative and quantitative changes as well as recalcitrant compounds not eliminable even under AOP treatment easily could be observed.

The combination of soft-ionizing APCI or ESI interface with MS and the addition of an excess of ammonium acetate for ionisation support in the positive mode produced either molecular ions or ammonium adduct ions ($[M+H]^+$ or $[M+NH_4]^+$). So an increase of complexity of spectra by generation of mixtures of adduct ions containing, in parallel, protons, and other cations such as sodium and potassium was avoided. With the application of pattern recognition to the standardized overview spectra in Fig. 4b–h, marginal or even dramatic qualitative and quantitative changes in the pollutant spectrum became obvious after the textile wastewater as shown in Fig. 4a had been submitted to various physicochemical, chemical, and AOP treatment procedures, respectively.

Without any further identification procedures we were sure that the high concentrations of the hardly biodegradable pollutants observed in untreated wastewater (Fig. 4a) were homologues of polyethylene glycol (PEG; Δ m/z 44; m/z 300, … 520) and non-ionic surfactants of alkylethoxylate type (AEO; Δ m/z 44; m/z 394, … 966) recognizable by their series of characteristic Δ m/z 44 equally-spaced ammonium adduct ions. In the samples treated by various physicochemical, chemical, and AOP treatment procedures, however, the screening approach of a visual assessment of the FIA-MS spectra allows to judge treatment efficiencies. The treatment of the textile wastewater with activated carbon (Fig. 4b) only led to changes in concentration compared to untreated sample (Fig. 4a) but no qualitative changes were recognizable in the pattern of ions. Comparable results in the elimination of polar compounds from the sample as shown in Fig. 4a but with minor variations could be observed for the treatment by ultrasonication (US) and US/UV as well as under hydrogen peroxide/UV or Fenton treatment. The application of O_3 or O_3/UV, however, led to a disappearance of the equally spaced Δ m/z 44 AEO homologues with ions between m/z 394 and 966 (Figs. 4f and 4g). In parallel compounds with Δ m/z 44 equally spaced ions between m/z 300 and 696 or 652, respectively, appeared in the spectra. While the concentration of these homologues under O_3/UV treatment was reduced (cf. Fig. 4g), an increase of the concentration of compounds with Δ m/z 44 equally spaced ions between m/z 300 and 696 could be observed under O_3 treatment (Fig. 4f). In parallel new compounds generated by O_3 or hydroxyl radical ($^{\bullet}OH$) oxidation of PEG or AEO could be observed, as shown in Fig. 5. When parts of overview spectra yet presented in Figs. 4a, d, f, and g were compared, new signals of ammonium adduct ions spaced with Δ m/z +14 or +28 from PEG ions at m/z 300, 344 and 388 can be recognized in the Figs. 5c and 5d. These patterns of signals were already reported by Schröder (9) when biological degradation of PEG and their precursor compounds—non-ionic surfactants of AEO type—also led to mono and di-carboxylated PEG homologues. As

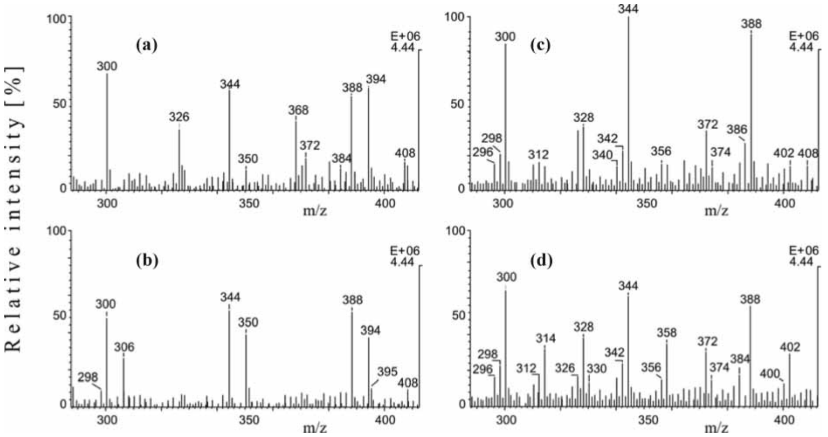

Figure 5. APCI-FIA-MS(+) loop injection spectra as in (Fig. 4((a) no treatment), ((b) US/UV−), ((c) O_3−) or ((d) O_3/UV treatment), extracted from Fig. 4(a)), (d), (f) or (g), respectively, and expanded for a visual recognition of qualitative and semi-quantitative changes in the ion patterns generated by different physicochemical oxidative treatment processes.

a result molar masses increasing by Δ m/z 14 or 28 were observable under O_3 or $^{\bullet}OH$ radical oxidation conditions.

This procedure of pattern recognition provided the information about the ions which could not be degraded by the different treatment techniques. However, as mentioned before, the knowledge about the compounds based on suppositions and therefore had to be confirmed. We tried to identify these compounds in a second step by generation of product ion spectra. In contrary to EI(+)-ionisation of volatile compounds after GC separation API interfaces generate molecular ions but no fragment ions essential for identification. By means of tandem mass spectrometry (MS-MS) using collision induced dissociation (CID) after FIA or in the LC mode product ions were generated. With the information about the molar masses of ions of concern obtained by FIA we tried to generate product ion spectra from these selected ions in the untreated wastewater which were recognized to be not or hardly eliminable from treated wastewater. After CID the pattern of fragments from product ion spectra were compared with product ion spectra of precursor ions contained in our laboratory-made product ion library. So identification could be achieved and, as we have guessed during FIA characterisation, the homologues with Δ m/z 44 equally spaced ions between m/z 300 and 520 were confirmed as PEG compounds after one of the prominent homologue ions at m/z 476 had been selected and fragmented (Fig. 6a). Homologue ions at m/z 394, . . . , 966, also Δ m/z 44 spaced, were identified as alkylethoxylate surfactant ($C_{13}H_{27}$-$(EO)_x$) compounds with varying numbers of PEG chain-links (Fig. 6b).

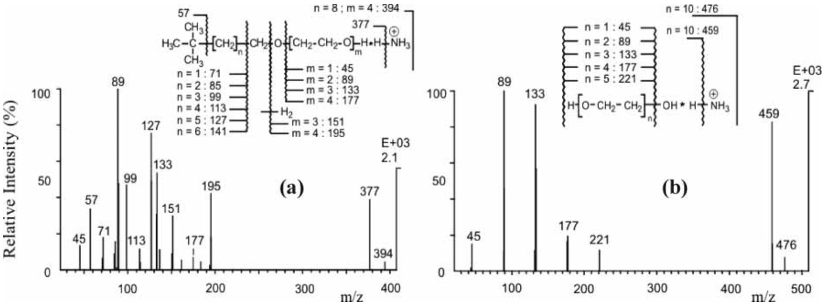

Figure 6. APCI-FIA-MS-MS(+) product-ion mass spectra obtained under CID conditions from selected unknown compounds in the untreated textile wastewater. Fragmentation schemes of precursor ions at m/z 394 and 476 in the insets confirmed their identification as ammonium adduct ions of (a) alkylethoxylate surfactant ($C_{13}H_{27}$-(EO)$_4$-O-H) or (b) PEG-homologue (H-(EO)$_{10}$-OH); (EO = -(O-CH_2-CH_2)-).

CONCLUSIONS

The degradation and/or elimination of organic pollutants contained in textile wastewater were found to be more or less effective according to the treatment technique applied. Sum parameter analyses indicated only marginal changes. To induce molecular destruction effects but no mineralization, small amounts of AOP reagents can be used. Under these conditions, the color disappeared, and DOC as well as COD decreased. In parallel a slight increase of BOD_5 could be achieved. The marginal increase of BOD is the result of the application of moderate quantities of oxidation reagents to a wastewater with an in parallel high load of dissolved organic compounds. The oxidized products of precursor pollutants destroyed by ozone or $^{\bullet}$OH radicals showed a reduced tendency in biodegradability but were not toxic to wastewater biocoenosis.

The results of the physicochemical treatment applying PAC, US, and US/UV were not effective in the destruction, elimination of pollutants by PAC adsorptions, however, this observation was worth mentioning. The determination of UV absorption proved that only under O_3 treatment (O_3 or O_3/UV) compounds with an aromatic organic structure preferentially were degraded observable as disappearance of the UV absorption at 250–300 nm as a result of the destruction of the chromophoric element, the aromatic ring system. The generation of $^{\bullet}$OH radicals by H_2O_2/UV or Fenton was not as effective as the application of comparable quantities of O_3. The application of these treatment techniques to biologically treated wastewater as an advanced treatment would lead to the elimination or degradation of recalcitrant compounds. The latter, more polar and potentially more toxic would be discharged untreated into the environment causing hazardous effects in surface water and drinking water treatment.

Substance-specific analyses, combined with MS detection for monitoring the elimination or degradation of volatile and/or polar pollutants, proved that elimination under O_3 or AOP treatment resulted in degradation reactions while physicochemical treatment in all cases either was non effective (US and US/UV) or led to an elimination by adsorption (PAC). O_3 or AOP treatment applying small reagent doses diminished volatile compounds generating polar compounds by oxidation while polar pollutants were destroyed or/and oxidation proceeded.

Chemical degradation could be followed up qualitatively and quantitatively by MS and could be qualitatively confirmed by MS/MS. Arising more polar constituents were characterized or identified as alcohol, carbonylic, or carboxylic type compounds. These processes led to compounds with the desired improved biodegradability while under US, US/UV, or PAC treatment no improvement in biodegradability was observed. Standardization of the TICs of GC/MS analyses (Fig. 3) and of the FIA/MS spectra (Fig. 4) allowed semi-quantitative estimations of conversion and elimination. Though no further adjustments of the pH conditions were performed to improve the oxidative potential of the reagents prior to treatment results obtained nevertheless were quite promising and therefore need more research.

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