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TEXTILE WASTEWATER REUSE: OZONATION OF MEMBRANE CONCENTRATED SECONDARY EFFLUENT

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ABSTRACT

Among the activities appointed by the EC research-project "Integrated water recycling and emission abatement in the textile industry" (Contract: ENV4-CT95-0064), the effectiveness of ozone for improving the biotreatability of recalcitrant effluents as well as for removing from them toxic and/or inhibitory pollutants has been evaluated at lab-scale. Real membrane concentrates (pH=7.9; TOC=190 ppm; COD=595 ppm; BOD₅=0 ppm; Conductivity=5,000 μ S/cm; Microtox-EC₂₀=34%) produced at Bulgarograsso (Italy) Wastewater Treatment Plant by nanofiltering biologically treated secondary textile effluents, have been treated with ozonated air (O₃conc.=12 ppm) over 120 min. The results have indicated that during ozonation, BOD₅ increases from 0 to 75 ppm, whereas COD and TOC both decrease by about 50% and 30 % respectively. As for potentially toxic and/or inhibitory pollutants such as dyes, nonionic surfactants and halogenated organics, all measured as sum parameters, removals higher than 90% were achieved as confirmed by the complete disappearance of acute toxicity in the treated streams. The only ozonation byproducts searched for and found were aldehydes whose total amount continuously increased in the first hour from 1.2 up to 11.8 ppm. Among them, formaldehyde, acetaldehyde, glyoxal, propionaldehyde, and butyraldehyde were identified by HPLC. © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

KEYWORDS

Biodegradability enhancement; membranes; ozone treatment; recalcitrant organics; textile wastewater.

INTRODUCTION

In Europe, increasing water consumption for industrial and domestic purposes is leading to potential water shortage within many Countries. European industry is also faced with increasing costs for the water it uses. A rational water resources policy would allocate the purest sources for potable use and develop effluent recycling processes for industrial consumption, where in most cases the quality requirements for micro-pollutants are less stringent.

Textile factories are among the largest industrial consumers of water. Therefore, textile industry, which is widespread throughout Europe, is a good candidate for development of intensive water recycling and minimization of related polluting emissions.

Effluents of textile processing plants contain numerous chemical substances from the major steps of desizing, dyeing, printing and finishing and are highly variable because of frequent changes of batch-type textile processing steps. The specific wastewater discharge is around 100-200 m³/ton of fabric while the average pollution is 100 kg COD/ton (Jekel, 1997). The input chemicals are usually pre-made mixtures of a large variety of major chemicals including high loads of salts required for dyeing. In particular, textile wastewater may include many types of dyes, detergents, insecticides, pesticides, fungicides, greases and oils, sulphide compounds, solvents, heavy metals, inorganic salts and fibres, in amounts depending on the processing regime. Among such chemicals, classes of concern are persistent dyes containing organic halogen-, sulfur- and nitrogen-radicals, polyphenols, sulfonated aromatic compounds and nonionic surfactants, such as nonylphenol ethoxylates (Shaul *et al.*, 1991; Camp and Sturrock, 1990). The recalcitrance and biotoxicity of most of these compounds together with their varying concentration and flow rate (Correia *et al.*, 1994) makes textile wastewater treatment quite problematic by conventional processes, either physico-chemical or biological, as such or in combination (Shelley *et al.*, 1976; Hamza and Hamoda, 1980; Shaul *et al.*, 1983; Grau, 1991). Therefore, as a considerable amount of these recalcitrant contaminants still remains in biologically treated textile effluents, important water savings may be obtained only by high efficiency treatment trains based on separation systems aimed to remove persistent pollutants and designed to recycle the major fraction of biologically treated effluents as purified water within the industries.

As a result of the great interest of European Countries about water savings in textile industry, a research project ("Integrated water recycling and emission abatement in the textile industry") has been financed by the European Commission (Contract: ENV4-CT95-0064) within the framework Programme IV: Environment and Climate 1994-1998. The project covers an integrated process for the provision of recycled water of guaranteed quality with minimum emissions. The whole process is divided in three modules, which are flexible in application and can be used separately or together. The first module is based on anaerobic digestion with a focus on dyes adsorption and heavy metals precipitation on anaerobic sludge. In the second module, biodegradable organics are removed and nitrogen compounds are oxidized by a biological aerobic stage. In the last module, the biologically treated wastewater is subjected to a final polishing for bringing the wastewater quality up to the standards required for reuse in textile industry. As polishing options, two separation processes are alternatively used: granular activated carbon adsorption or membrane filtration (Rozzi *et al.*, 1997).

The latter option, regardless of the used membrane technology (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), produces in addition to filtered effluents (permeates) fully recyclable in textile processing, membrane concentrates containing a high amount of recalcitrant organics that must be disposed of. To avoid this "plant-emission", a possibility is to recycle the concentrates back to the biological aerobic stage but this would cause a continuous increase of recalcitrant and toxic or inhibitory pollutants concentration in the activated sludge basin. In order to overcome such a drawback, it has been proposed that, before being recycled back, membrane concentrates are first treated with ozone. In the last few years, in fact, ozonation has been reported as a chemical oxidation treatment potentially effective for improving the biotreatability of wastewater characterized by a high content of non-biodegradable and toxic components (Qian *et al.*, 1994; Jochimsen *et al.*, 1997). From the chemical stand point, such a biotreatability enhancement is ascribed to the partial oxidation of recalcitrant pollutants into more easily biodegradable intermediates as well as to the degradation of toxic pollutants that inhibit biomass activity (Gilbert, 1987; Nobuyuki *et al.*, 1994; Lopez *et al.*, 1998).

The present paper reports the results of a lab-scale investigation, carried out within the framework of the above European Project, specifically aimed to check the effectiveness and the reliability of such an ozonation by treating real membrane concentrates produced by nanofiltration of secondary textile effluents at Bulgarograsso (Como-Italy) Wastewater Treatment Plant.

METHODS

Wastewater. The investigation has been carried out using the concentrates produced by nanofiltering the secondary effluents discharged by the Bulgarograsso (Como-Italy) combined wastewater treatment plant (80/20 textile/domestic organic load and 70/30 hydraulic flow rate respectively). The plant consists of a conventional activated sludge tank with a pre-denitrification reactor, and it is sized for 25,000 m³/d dry weather flow. The choice of the combined treatment is due to local conditions: many textile printing and dyeing factories using the same technologies are concentrated in the served area. Therefore their effluents are collected in the sewerage system, mixed with the local domestic wastewater that provide the nutrients lacking from the industrial effluents and necessary for biological aerobic processes, and treated in centralized treatment plants.

Membrane-filtration. Secondary effluents nanofiltration was carried out by a pilot unit including two spiral wound membrane modules that can produce 300 l/h of permeate. The unit is equipped with a high pressure pump (up to 40 bar), three flow meters (permeate, concentrate and drain), a thermometer (feed) and 3 conductivity-meters (feed, permeate and concentrate). The unit is located in a container together with the necessary tanks for the washing operation. The nanofiltration module (Separem, Biella/Italy) used in the pilot scale unit is a spiral wound composite polyamide membrane (Molecular Weight Cut Off = 150 dalton; Surface = 8.36 m²; Min. rejection MgSO₄: 96%) deposited on a polysulphone support with an operating pressure of 10 bar and a maximum temperature of 50°C. This type of membrane allows one to separate low molecular weight compounds and divalent salts, reducing the hardness of the filtered solution.

Ozonation. Ozone was produced from air by a Fisher 502 generator (Fisher, Meckenheim/Bonn, Germany) and continuously bubbled, at a flow rate of 60 l/h, into a Normag mod. A9316 (Normag, Hofheim am Taunus, Germany) batch-reactor filled with 0.4 l of the sample to be treated. Ozonation was carried out, at room temperature, and, at scheduled times, ozonated samples were quenched by adding the appropriate volume of 0.5M sodium thiosulfate solution.

Analyses. Aldehydes were measured both spectrophotometrically as sum parameter, expressed as formaldehyde (HCHO), according to Italian standard methods (Istituto di Ricerca Sulle Acque, 1994) and by HPLC-UV as specific compounds according to the EPA method 8315 (Environmental Protection Agency, 1992). The used instruments were respectively an UV-Vis. Varian spectrophotometer (Mod. Cary 1-E) and a Varian 9012 gradient pump equipped with a Varian 9070 UV detector (Varian, Palo Alto/CA-USA).

TOC (Total Organic Carbon) content was measured by a 5050 TOC analyser (Shimadzu Co, Japan). NPDOX (NonPurgeable Dissolved Organic Halogens) content was measured by a microcoulometric ECS 1000 Analyzer (Euroglas BV, Delft/The Netherlands) and expressed as ppm of organic-chloride (mg Cl/l).

Acute toxicity was measured as Effective Concentration (EC₂₀) [i.e., the sample concentration that results in a 20 percent reduction of the light emitted by appropriate bioluminescent bacteria after a contact time of 30 min] by a Microtox analyzer Mod.500 (Azur Environmental, Carlsbad/CA-USA).

Referring to surfactants, as preliminary analyses indicated that most of them (>80%) were nonionic, only this class was searched and measured, as ppm of a standard reference-surfactant, by a two phases titration with the Tetrakis reagent according to a simplified method for their determination in presence of anionic surfactants (Tsubouchi *et al.*, 1985).

As for colour, according to standard procedures, it was measured as sample absorbance at three visible wavelengths (660, 558, and 426 nm) in 1 cm absorption cell. However, as the latter wavelength was the dominant, in the text it was the only one reported. The other parameters not specified above, were analyzed according to the relative standardized procedure (Standard Methods, 1995).

RESULTS AND DISCUSSION

Table 1 reports the main characteristics of investigated membrane nanofiltered textile secondary effluents.

Table 1. Average values of the main parameters of investigated streams

pH	Cond.	TOC	COD	BOD ₅	TSS	Colour λ=426nm	Cl ⁻	NPDOX	Nonionic Surfactants	Aldehydes as HCHO	EC ₂₀ (30min)
	μS/cm	MgC/l	MgO ₂ /l	mgO ₂ /l	mg/l	Abs(1cm)	g/l	μgCl/l	mg/l	mg/l	(%)
7.95	5,000	190	595	0	50	0.502	1.0	789	6.29	1.24	34

The generally high values reported in this table clearly indicate the strong polluting impact of such streams. As for the values of sum parameters (Color, NPDOX, Surfactants) representing specific classes of toxic and/or inhibitory pollutants, respectively: dyes, halogenated organics and nonionic surfactants, they certainly contribute to the acute toxicity value (34%) expressed as EC₂₀. The occurrence of recalcitrant and or inhibitory pollutants in the considered streams is additionally confirmed by the high TOC and COD values, respectively 190 and 595 ppm, to which corresponds a BOD₅ value of zero.

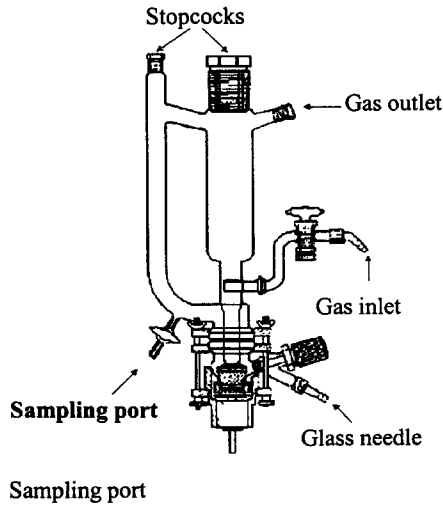


Figure 1. Sketch of ozonation batch reactor.

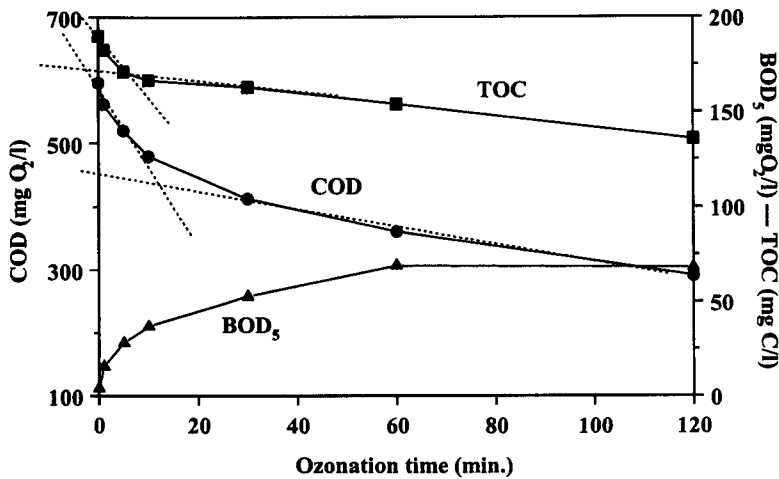


Figure 2. TOC, COD and BOD₅ trends during ozonation.

As for Figures 1 and 2, they respectively show a sketch of the used ozonation batch-reactor and the TOC, COD and BOD₅ trends measured during ozonation .

The results shown in Figure 2 demonstrate the effectiveness of the ozonation treatment. In fact, during such a treatment BOD₅ value increases from zero to 75 ppm. Simultaneously TOC and COD decrease respectively from 190 to 135 ppm (i.e., 29%) and from 595 to 290 ppm (i.e., 51%) even though a sharp reduction of their decreasing-rate seems to occur after the first 20 min as indicated by the slopes of the dotted lines. This is presumably due to the great variability of reaction rate constants (k as $M^{-1}s^{-1}$) of ozone with different classes of organic compounds [e.g.: hydroquinones ($k \approx 10^6$); phenols ($k \approx 10^3$); benzene ($k \approx 1$); alcohols ($k \approx 10^{-2}$); carboxylic acids ($k \approx 10^{-3}$)] (Hoigné and Bader, 1983a,b).

Even though TOC decrease is mainly due to the chemical oxidation of organic carbon to CO₂ and/or to carbonates (CO₃²⁻/HCO₃⁻), a minor additional contribution of physical TOC removal should be also taken into account. In fact among the numerous intermediates formed during the progressive oxidation of organics to CO₂, the more volatile could be stripped out from the reactor by the ozonated air continuously bubbled into it. However, even though such additional contribution has not been quantified, on the basis of stripping theory, it should be minimal and easily avoidable by appropriate reactor design (McCarty, 1987).

As for COD removal, the amount of its extent can be considered as the sum of two contributions: a major one due to the corresponding TOC reduction (i.e., to the complete oxidation of organics to CO₂) and a second one associated with the partial oxidation of organic substrates. It is just this partial oxidation that causes the transformation of recalcitrant pollutants into more biodegradable derivatives as well as the consequent BOD₅ increase shown in figure 2, and whose amount provides a rather accurate indication about the real extent of the biotreatability enhancement achievable by ozonation.

Figure 3 shows the trends, recorded during ozonation, of sum-parameters (surfactants, NPDOX, colour and total aldehydes) representing specific classes of recalcitrant pollutants potentially toxic and/or inhibitory, respectively: nonionic surfactants, halogenated organics, dyes and aldehydes.

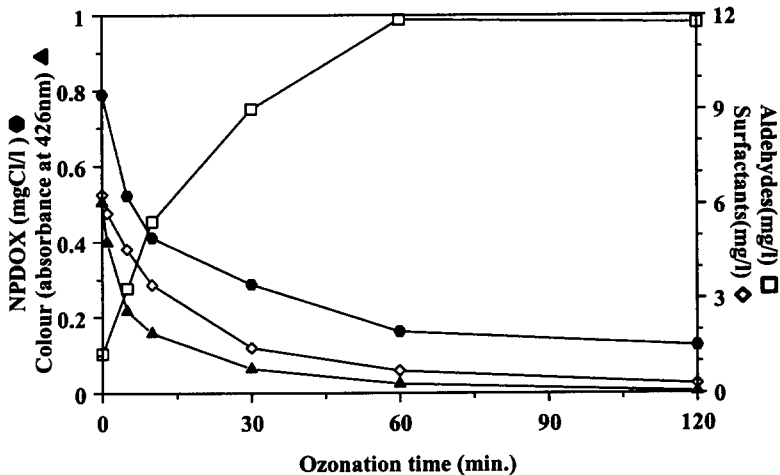


Figure 3. Trends of sum-parameters referring to toxic and/or inhibitory pollutants during ozonation. (Analytical methods are reported in the Methods section).

Except for aldehydes, the data in Figure 3 essentially point out the great effectiveness of ozonation for degrading the considered pollutants. In particular, as for halogenated organics, on the basis of thermodynamic considerations, their concentration, measured as NPDOX, was expected to increase during ozonation. In fact, as the oxidation potential of ozone ($E^{\circ} = 2.07$ volts) is greater than that of chlorine ($E^{\circ} = 1.39$ volts), it could be reasonably guessed that chloride ions occurring in the membrane concentrated streams (about 1,000 ppm) should be easily oxidized by ozone to form chlorine (Cl₂). This, in turn, should

rapidly react with the organic substances (TOC) occurring in the same streams to form halogenated organic derivatives (NPDOX). The opposite trend shown in Figure 3 proves that in spite of the favorable $\text{ox} \leftrightarrow \text{red}$ conditions, chlorides oxidation does not take place, presumably because of kinetics constrains (Kiwi and Gratzel, 1981), avoiding the formation of further halogenated organics.

In addition, the same figure shows that, as expected, aldehydes, measured as sum parameter and expressed as ppm of formaldehyde, really represent a quantitatively relevant class of ozonation byproducts. Their concentration, in fact, continuously increases up to 60 min, and soon afterwards slightly decreases presumably because of the above discussed stripping effect. By HPLC analyses of single aldehydes, carried out according to the EPA method mentioned in the previous section, formaldehyde, acetaldehyde, glyoxal, propionaldehyde and butyraldehyde have been identified. Their max average concentrations resulted respectively 5.41, 0.23, 0.91, 0.05 and 0.01 ppm. Formaldehyde and acetaldehyde, however, were found even in untreated streams at an average concentration of 0.37 and 0.02 ppm respectively.

Acute toxicity of streams was measured before and after ozonation. As for untreated streams, the resulting average value, expressed as EC_{20} , was 34%. In other words, to achieve a 20 percent reduction of the light emitted by bioluminescent bacteria after a contact time of 30 min, samples of untreated streams (34 ml) must be diluted with distilled water (76 ml). On the contrary, EC_{20} measures referring to ozonated streams, at 60 and 120 minutes, indicated that such samples were not toxic. This means that even contacting undiluted samples with bioluminescent bacteria no reduction of the emitted light took place at all. Such a complete toxicity abatement indicates that in spite of aldehydes concentration increase, as shown in figure 3, the major role in influencing the toxicity trend is due to the corresponding decrease of other potentially toxic pollutants such as dyes, surfactants and halogenated organics. This is indirectly confirmed also by the continuously increasing BOD_5 trend shown in Figure 2, possibly caused by the degradation of xenobiotic pollutants that potentially inhibit biomass activity (Scott and Ollis, 1995).

CONCLUSIONS

An experimental investigation aimed to assess the effectiveness of ozone-treatment for improving the biodegradability of recalcitrant effluents and for degrading potentially toxic and/or inhibitory pollutants occurring in the same streams, has been carried out at lab-scale by treating real membrane concentrates produced, by nanofiltration of biologically treated textile effluents, at Bulgarograsso (Italy) Wastewater Treatment Plant. The main conclusions that can be drawn on the basis of the results obtained under the used experimental conditions, are the following:

- Biodegradability enhancement of the investigated streams has been truly achieved as BOD_5 increases from 0 to 75 ppm;
- Significant TOC and COD removals, respectively 29% and 51%, were also accomplished even though a minor contribution of physical removal by stripping has to be taken into account;
- Ozonation also causes a relevant reduction, close to 90%, of all the values of the sum-parameters referring to specific classes of potentially toxic and/or inhibitory pollutants (dyes, halogenated organics, nonionic surfactants) as confirmed by the lack of any acute toxicity in ozonated samples. On the contrary, untreated samples toxicity was 34% as EC_{20} at 30 min;
- In spite of the high concentration of chloride ions in untreated streams (about 1,000 ppm) and the favorable thermodynamic conditions [i.e., the oxidation potential of ozone ($E^\circ = 2.07$ volts) greater than that of chlorine ($E^\circ = 1.39$ volts)], chloride oxidation to chlorine does not take place because of kinetic constraints. This avoids the undesired formation of halogenated organic byproducts as a result of the possible fast reaction between chlorine and organic matter (TOC);
- As expected, aldehydes, the most likely ozonation byproducts, have been searched for and found. Their total concentration continuously increases during ozonation from 1.2 to 11.8 ppm. Among them, glyoxal, formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde, have been identified by HPLC-UV analyses.

In conclusion, ozone treatment is quite effective for achieving all the objectives scheduled at the beginning of the present investigation.

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