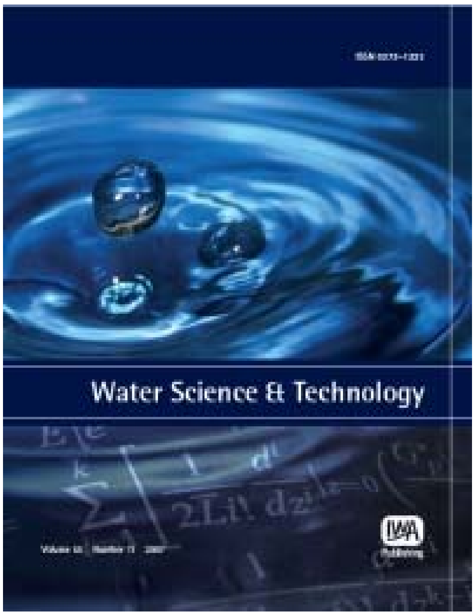
Water Science & Technology

Reduction of organic trace compounds and fresh water consumption by recovery of advanced oxidation processes treated industrial wastewater

S. Bierbaum, H.-J. Öller, A. Kersten and A. Krivograd Klemenčič

ABSTRACT

Ozone (O_3) has been used successfully in advanced wastewater treatment in paper mills, other sectors and municipalities. To solve the water problems of regions lacking fresh water, wastewater treated by advanced oxidation processes (AOPs) can substitute fresh water in highly water-consuming industries. Results of this study have shown that paper strength properties are not impaired and whiteness is slightly impaired only when reusing paper mill wastewater. Furthermore, organic trace compounds are becoming an issue in the German paper industry. The results of this study have shown that AOPs are capable of improving wastewater quality by reducing organic load, colour and organic trace compounds.

Key words | advanced oxidation processes (AOPs), organic trace compounds, pulp and paper industry, textile industry, water reuse, wastewater

S. Bierbaum (corresponding author)
H.-J. Öller
Papiertechnische Stiftung,
Hess-Str. 134, 80797 Munich,
Germany
E-mail: *svenja.bierbaum@ptspaper.de*

A. Kersten
Institution for Paper Science and Technology-gGmbH,
Alexanderstr. 8,
64283 Darmstadt,
Germany

A. Krivograd Klemenčič
Institute for Water of the Republic of Slovenia,
Hajdrihova 28c, 1000 Ljubljana,
Slovenia
and
University of Ljubljana,
Faculty of Health Sciences,
Zdravstvena pot 5, 1000 Ljubljana,
Slovenia

INTRODUCTION

The limitations of conventional wastewater treatment methods for industrial wastewater (van der Zee & Villaverde 2005) may require an advanced treatment technology. More and more research focuses on combining biological treatment with other techniques such as advanced oxidation processes (AOPs) to ensure a cost-effective technology (Hai *et al.* 2007; Mahne 2012) that reduces pollution. Especially if treated wastewater is to be reused, extensive removal of organic loads as well as almost complete decolourization is necessary. Research results and the operation of large-scale plants have shown that the organic load can be reduced by up to 90% by combining ozone treatment with a subsequent biological low load stage; reduction rates of 50% and below are economically worthwhile (Schmidt & Lange 2000; Bierbaum 2010; Kaindl 2011). Moreover, several parameters such as organic load, colour and adsorbable organic halogens are positively affected by ozone.

Regions lacking fresh water require new water sources. Several recommendations and evaluations of the potentials of cascading water use to substitute fresh water can be found (Visvanathan & Asano 2001; Durham *et al.* 2005; Angelakis & Durham 2007). It is already being practised in some cases (Jacobsen 2006; Blanco *et al.* 2009; Lazarova 2013). This is why studies have been carried out to tap new sources for highly water-consuming industries by re-using AOP and biologically treated wastewater. The preconditions are an efficient AOP treatment to ensure optimum water quality at affordable costs, and a demonstration that the use of treated wastewater is possible. Wastewater is provided by paper mills, food and textile producers and municipalities, to be reused in paper mills and textile factories. The accumulation of salts in water circuits is a problem if paper mills reuse their own wastewater. Cascading water use, which uses water from elsewhere, has been investigated to avoid this problem.

To an ever greater extent, German paper mills must have their wastewater tested for organic trace compounds. The reasons for this are the Water Framework Directive, the Directive on Environmental Quality Standards and the German Surface Water Ordinance, whose declared aim is to reduce or even totally eliminate the discharge of certain organic trace compounds. The concentrations of these compounds in paper industry wastewater can be reduced by AOPs, but there is a lack of knowledge about the ability of

doi: 10.2166/wst.2013.569

AOPs to simultaneously reduce different kinds of critical trace compounds (Fontanier *et al.* 2005). In paper mill wastewater, among others, complexing agents such as diethylene triamine pentaacetic acid (DTPA), polycyclic aromatic hydrocarbons (PAH) and chlorinated aromatic hydrocarbons (CAH) as well as bisphenol A (BPA) are most in focus (Kersten *et al.* 2006; Hamm *et al.* 2007).

Table 1 | Parameters used for trials with paper mill wastewater

Trials	Dosages/Settings
Ozone 1	0.25 g O_3/g COD_0
Ozone 2	0.5 g O_3/g COD_0
Ozone+ UV	0.5 g O_3/g COD_0, 20 kWh/m³
UV 1	5 kWh/m³
UV 2	10 kWh/m³
UV + H_2O_2 1	5 kWh/m³, 0.75 g H_2O_2/g COD_0
UV + H_2O_2 2	10 kWh/m³, 0.75 g H_2O_2/g COD_0
Fenton 1	1 g H_2O_2/g COD_0, 10 g H_2O_2/g Fe^{2+}
Fenton 2	2 g H_2O_2/g COD_0, 40 g H_2O_2/g Fe^{2+}
Photo Fenton 1	1 g H_2O_2/g COD_0, 10 g H_2O_2/g Fe^{2+} + 5 kWh/m³
Photo Fenton 2	1 g H_2O_2/g COD_0, 10 g H_2O_2/g Fe^{2+} + 10 kWh/m³
Membrane	7 bar, 30 °C
Activated carbon	5 g/L, agitating 120 min

The aim of this study was to test different combinations of AOPs for the treatment of paper mill and textile wastewater to find out which combination is most efficient for removing colour, chemical oxygen demand (COD) and organic trace compounds and to assess the impact of water reuse in paper production on product quality.

MATERIALS AND METHODS

AOP and reference trials

Fully biologically treated wastewater from two typical paper mills using 100% paper for recycling as raw material and raw wastewater from one textile factory producing socks and stockings were subjected to laboratory-scale AOP and reference trials. Table 1 shows the dosages and settings used for the paper mill wastewater, COD_0 being the COD in the original, untreated samples and UV being ultraviolet treatment. To take account of different levels of COD_0 in the tested water, dosages have been calculated as relative values per g COD_0. The settings were chosen based on the experience of the authors and values in the literature.

Ozone trials

Ozone trials were performed with a laboratory ozone plant (Figure 1, top) having a maximum ozone production in air

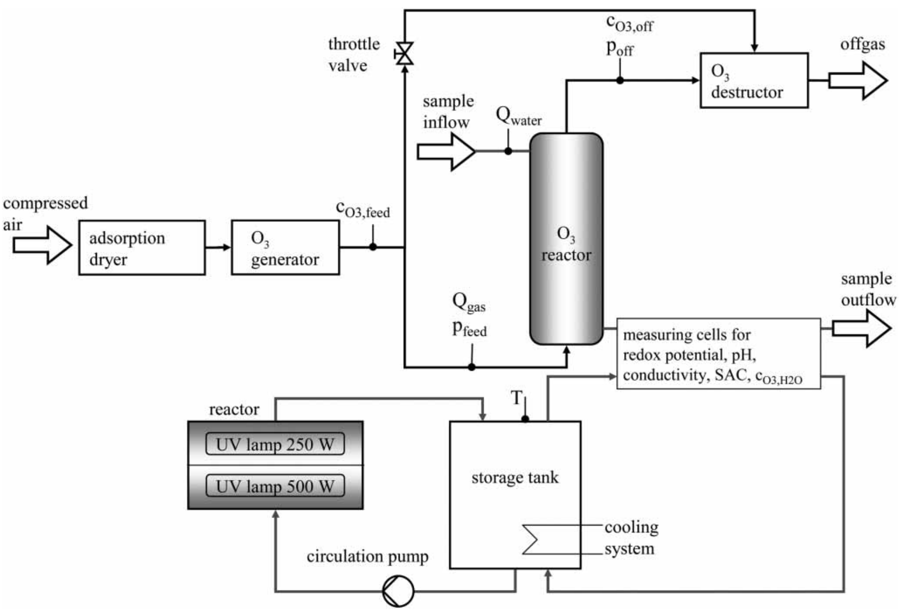

Figure 1 | Schematic of the laboratory ozone plant (top) and UV plant (bottom).

of 25 g/h, gas flow rate (Q_{gas}) of 60 L/h, and water flow rate (Q_{water}) of 2–10 L/h. Ozone dosages varied between 12–130 g/m^3. In the reactor, the ozone-containing gas is passed over a frit and rises through the water to be ozonised. Part of the ozone contained in the gas diffuses into the water, is dissolved and reacts with the substances contained in the water. The ozone destructor destroys ozone that has remained in the gas. Measurements of pressure (p_{feed}, p_{off}) and ozone concentration in feed- and offgas ($c_{O3,feed}$, $c_{O3,off}$) as well as of gas and water flow rates serve to balance the ozone dosage introduced into the sample. The water to be ozonised is pumped through the reactor in counter-current mode. The sample is supplied to measuring cells to determine the conductivity, pH, redox potential, spectral absorption coefficient at 254 nm ($SAC_{254\,nm}$) and ozone concentration in water. All values were logged at intervals of 10 seconds.

UV trials

UV trials were performed with a laboratory UV plant (Figure 1, bottom). The plant comprised two UV medium pressure lamps of 250 and 500 W, and a 20 L storage tank. The water was pumped from the storage tank in a circuit around the UV lamps. For UV + H_2O_2 trials, hydrogen peroxide (H_2O_2) (30%) was added prior to UV irradiation. As in the ozone trials, the water was passed through the measuring cells and values were logged every 10 seconds.

Fenton and photo-Fenton trials

Fenton trials were performed as jar tests. First, ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) was added to the sample, the pH was adjusted to <3 using HCl, and then H_2O_2 (30%) was added. The mixture was stirred for up to 16 hours. The sample was neutralised with sodium hydroxide prior to analysis. The mixture prepared for the photo-Fenton trials was circulated around the 250 W UV lamp for 15–30 minutes and neutralised afterwards.

Reference trials

Reference trials were performed with a membrane and activated carbon (AC). The following DOW NF90 nanofiltration membrane was used: polyamide thin-film composite; cut-off 90 Da; stabilized salt rejection NaCl 85–95%. The characteristics of the powdered activated carbon Norit SX PLUS were as follows: iodine number: 1050; molasses number (EUR): 215; methylene blue adsorption 22 g/100 g; total surface area (B.E.T.) 110 m²/g; apparent density (tamped) 350 kg/m³; particle size D_{10}: 6 µm; particle size D_{50}: 20 µm; particle size D_{90}: 80 µm.

Organic trace compounds

Measured values of organic trace compounds contained in wastewater samples from the selected paper mills were mostly close to or below the detection limit of the measuring method. For comparable conditions and to better assess the effectiveness of the processes, the wastewater samples were enriched with organic trace compounds. The following amounts were added:

- Complexing agents: 5 mg/L per substance
- BPA: 100 ng/L
- PAH: 200 ng/L per substance
- CAH: 200 ng/L per substance.

Impact of water reuse on product quality

To estimate the influence of reuse and subsequent use of AOP treated wastewater on paper quality, sheet former

Table 2 | Scenarios for sheet former trials

Scenario	Source of wastewater	AOP treatment	Share of AOP-treated wastewater	Share of white water 1
Ref.	–	–	0%	100%
Sc_1	Paper industry	Ozone	50%	50%
Sc_2			100%	0%
Sc_3	Food processing industry	Ozone	50%	50%
Sc_4			100%	0%
Sc_5	Municipal wastewater	Ozone + UV	50%	50%
Sc_6			100%	0%

trials (Table 2) were performed. Processes and settings that proved to be most effective in prior trials (data not shown) were chosen for each source of wastewater to produce water for sheet former trials. Original process water (white water 1; WW 1) was used to show the current situation in paper mills, and these results serve as the reference (Ref.). The exclusive use of AOP-treated wastewater from the selected sectors is the worst case scenario (Sc), whereas the mixed scenario represents possible water reuse.

Analytics

Standard analytics

Table 3 shows the methods used for water and paper measurements.

Organic trace compounds

Complexing agents were determined according to DIN 38413–8:2000–09. Samples for gas chromatography coupled with mass spectrometric detection (GC/MS) were prepared by Stir Bar Sorptive Extraction and subsequent thermodesorption prior to measuring the organic trace compounds (PAH, CAH and BPA) in the lower concentration range of ng/L. This method is based on the accumulation of organic compounds in the polydimethylsiloxane layer covering the magnetic stir bar. The trace compound analysis method was adapted to the complex matrix of paper mill wastewater (Baltussen *et al.* 1999).

Table 3 | Analytical methods

Parameter (water)	Method
COD	DIN ISO 15705
Colour	DIN EN ISO 7887

Parameter (paper)	Method
Bending stiffness	DIN 53 121
Breaking elongation, tensile strength, modulus of elasticity	DIN EN ISO 1924-2
Colour as L*a*b*-values	CIE LAB System

RESULTS AND DISCUSSION

AOP trials

Comparison of paper mill and textile factory wastewater

Figure 2 shows the remaining COD shares and colour values measured as the spectral absorption coefficient at 436 nm ($\alpha_{436\,nm}$) for three AOPs or combinations. The colour measured at 436 nm is evaluated here because this wavelength represents the typical yellow-brownish colour of paper mill wastewater. This yellow-brownish colour may cause problems when producing white paper. The same wavelength was evaluated for textile wastewater for reasons of comparability. Comparison is made between paper mill and textile factory wastewater. The paper mill wastewater differ significantly from textile factory wastewater (paper mill wastewater: COD: 135–160 mg/L, $\alpha_{436\,nm}$: 10–14 m^{-1}; raw textile wastewater: COD: 660–760 mg/L, $\alpha_{436\,nm}$: 28–74 m^{-1}).

The COD and colour of both paper mill and textile wastewater were reduced by AOP treatment. The most effective AOP in terms of COD and colour reduction among the three AOPs compared here was ozone for paper mill wastewater. Additional UV treatment did not show any improvement. Whereas for textile factory wastewater, the combination of ozone and UV treatment proved to be the most efficient combination, UV + H_2O_2 treatment showed poor efficiency for paper mill wastewater and better efficiency for textile wastewater.

Organic trace compounds

Figure 3 shows the elimination of trace compounds by AOPs and reference processes. All trials were performed with the

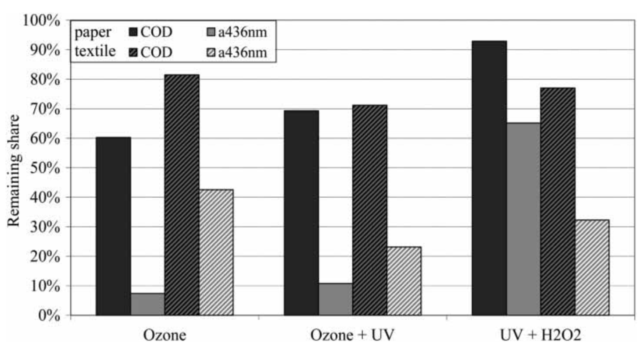

Figure 2 | Remaining shares of COD and colour achieved in paper mill and textile factory wastewater.

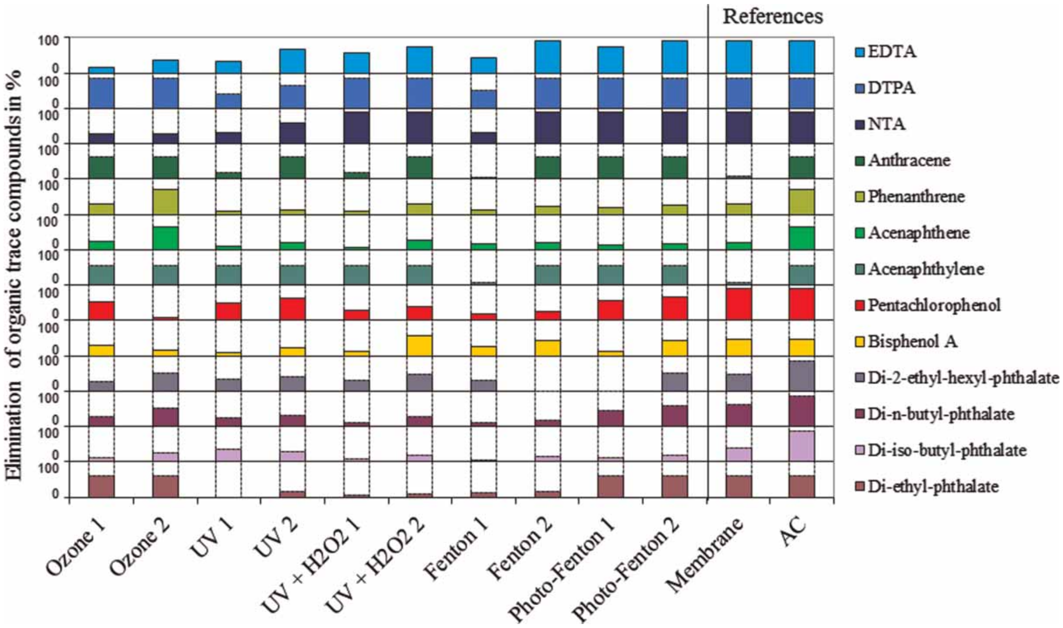

Figure 3 | Elimination of trace compounds achieved by AOPs and reference processes.

same paper mill wastewater sample (COD 220 mg/L, $\alpha_{436\,nm}$ 17 m^{-1}). The following substance classes were represented: complexing agents (ethylene diamine tetraacetic acid, (EDTA), DTPA, nitrilotriacetic acid (NTA)), PAH (anthracene, phenanthrene, acenaphthene, acenaphthylene), pentachlorophenol (PCP) as a representative of CAH, BPA and phthalates (di-2-ethyl-hexyl-phthalate, di-n-butyl-phthalate, di-iso-butyl-phthalate, di-ethyl-phthalate).

The trace compound elimination rates rose consistently in direct proportion to the treatment intensity (oxidant dosage, energy input). The greatest increase, i.e. doubling of the overall elimination rate, was shown in Fenton trials after doubling the peroxide dosage (Fenton 1: 1 g H_2O_2/g COD_0; Fenton 2: 2 g H_2O_2/g COD_0). Further dosage optimisation increased the overall elimination rate to 71%. Combining processes also increased the overall elimination rate, e.g. photo-Fenton treatment yields overall elimination rates of 37–51%, compared to 16–34% achieved by Fenton treatment alone. Thus, overall elimination rates close to the reference treatment process, activated carbon (up to 80%), were achieved.

Trace substances with absorption bands in the UV range can be eliminated very well by UV radiation with high energy input. This applies in particular to PCP and PAH as well as to the phthalates. Processes that use H_2O_2 are preferable for the preferential elimination of bisphenol A compared to ozone and UV treatment. Both the energy input and the H_2O_2 dosage, however, must be well balanced. Additional trials were performed for their optimisation, but are not part of this paper.

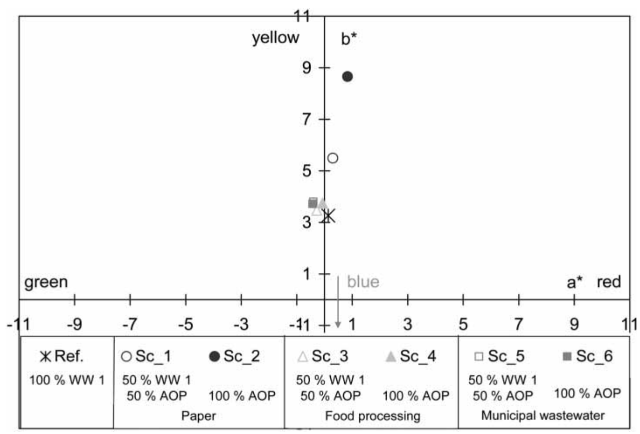

Figure 4 | Colour coordinates of handsheets produced with AOP treated water.

Impact of water reuse on product quality

Colour coordinates

The a*b*-plane of the CIE L*a*b* colour system in Figure 4 shows the influence of water use on the colour of handsheets, with a*- and b*-values of absolutely white paper sheets serving as zero.

The results of 100% white water (WW) use reflect the current situation in paper mills, thus serving as a reference. The use of both AOP-treated food processing and municipal wastewater yields the same colour coordinates of handsheets as the reference, at a proportion of both 50% and even 100% wastewater use. Hence, the reuse of these waters does not impair the whiteness of paper. The handsheets produced with AOP treated paper mill wastewater, however, did indeed show a slightly yellowish colour that increases with the proportion of wastewater used. This is due to the yellowish colour of paper mill wastewater remaining after AOP treatment. Thus, the reuse of this water for papermaking should be considered by mills producing brown papers.

Mechanical properties

Compared to the use of WW, the use of AOP treated wastewater did not impair the strength properties of handsheets (analysed according to Table 3) in all cases investigated. There was even an increase in strength with an increased proportion of AOP-treated wastewater. This effect was observed for all wastewaters used. The reason might be the lower load of treated wastewater compared to WW. It can therefore be concluded that the reuse of AOP-treated wastewater for the tested sectors in paper production does not impair the mechanical properties.

ECONOMICAL COST ASSESSMENT OF TESTED PROCESSES

To assess the operation costs of the advanced treatment of paper mill wastewater by selected processes, oxidant dosage, energy input and sludge disposal were considered. Operating costs for the purpose of reducing organic loads by ozone would add up to 2.90 €/kg COD_{eli} (0.20 €/m^3), including a subsequent biofilter. Adding H_2O_2 enhances the effect of ozone without high additional costs, thus amounting to 2.80 €/kg COD_{eli} (0.20 €/m^3). The removal of organic load from raw textile wastewater by ozone and UV treatment would cost 1.00 €/kg COD_{eli}. Operating costs for the removal of trace compounds from paper mill wastewater by Fenton treatment are broad, ranging between 0.45 and 7.50 €/m^3, due to considerable differences in the amount of sludge. Costs for the treatment by UV + H_2O_2 or by activated carbon are in the region of 1.00 €/m^3. Operating a downstream biofilter would cost 0.02 €/m^3 in addition. By comparison, the operating costs of paper mills' conventional wastewater treatment plants range between 0.05 and 2.35 €/m^3 with a mean value of 0.45 €/m^3 (Jung *et al.* 2011). Substitution of fresh water by treated wastewater can reduce these costs in the form of saved fresh water fees.

CONCLUSIONS

Based on the results achieved, it can be stated that AOP treatment improves the quality of fully biologically treated paper mill wastewater and raw textile wastewater regarding organic load and colour. Basically, paper mill wastewater shows only very low concentrations of critical organic trace compounds. The tested processes showed different elimination rates for the trace compound classes studied. Appropriate combinations of AOPs as well as enhanced treatment intensity may increase the effect. Which process or combination of processes is the most effective depends on the water to be treated, on the target compound to be eliminated and the water quality requirements. The reuse of AOP-treated paper mill, food processing and municipal wastewater in paper mill production processes does not impair the strength properties of paper. Paper whiteness is slightly impaired only when reusing paper mill wastewater that has not been fully decolourised.

An overall assessment will be necessary on a case-by-case basis to develop a specific advanced treatment concept which takes into account the following aspects:

- elimination of all critical organic trace compounds, but also of preferred single compounds;
- elimination of organic load;
- efficiency of the advanced treatment step combined with a subsequent biological degradation step; and
- operating and investment costs considering the reuse of treated wastewater.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the German Federal Ministry of Economics and Technology BMWi for funding the research project IGF 16552N, as well as to the German Federal Ministry of Economics and Technology BMWi, the Slovenian Ministry of Higher Education, Science and Technology (MVZT) and other funding agencies for funding CORNET project 46 EN 'AOP4Water' (www.cornet-aop4water.eu). Most of the results shown were findings revealed by these two projects. Special thanks are also extended to the paper mills and textile factories involved for supplying the wastewater samples and supporting the factory investigations.

REFERENCES

Angelakis, A. N. & Durham, D. 2007 Wastewater reclamation and reuse in EUREAU countries: trends and challenges. *Desalination* **218** (1–3), 3–12.

Baltussen, E., Sandra, P., David, F. & Cramers, C. 1999 Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: theory and principles. *Journal of Microcolumn Separations* **11** (10), 737–747.

Bierbaum, S. 2010 Use of Ozone Technology for the Advanced Treatment of Wastewater from Productions Using no Recovered paper, Report, PTS, Munich, Germany.

Blanco, Á., Negro, C., Ordóñez, R. & San Pío, I. 2009 Requirements of reclaimed water to be used as fresh water for paper manufacturing – case example Holmen Paper Madrid. In *PTS Symposium 'Water and Environmental Technology – New Concepts to Meet Future Challenges'*, (H.-J. Öller & A. Hutter, eds) PTS, Munich, Germany, 2009, proceedings PTS-WU 908.

Durham, B., Angelakis, A. N., Wintgens, T., Thoeye, C. & Sala, L. 2005 Water Recycling and Reuse. A Water Scarcity Best Practice Solution. Technical paper, Environmental Technologies of the European Environment Agency. Available at: http://technologies.ew.eea.europa.eu/technologies/resourc_mngt/water_use/Water_recycling_and_reuse_a_water_scarcity_solution._Final.doc (accessed 05/08/2013).

Fontanier, V., Farines, V., Albet, J., Baig, S. & Molinier, J. 2005 Oxidation of organic pollutants of water to mineralization by catalytic ozonation. *Ozone: Science and Engineering* **27** (2), 115–128.

Hai, F. I., Yamamoto, K. & Fukushi, K. 2007 Hybrid treatment systems for dye wastewater. *Critical Reviews in Environmental Science and Technology* **37**, 315–377.

Hamm, U., Schabel, S. & Öller, H.-J. 2007 Comparison of the endocrine effects of treated wastewaters from different paper mills by use of an in-vitro test with modified yeast cells. *Water Science and Technology* **55** (6), 213–221.

Jacobsen, N. B. 2006 Industrial symbiosis in Kalundborg, Denmark – a quantitative assessment of economic and environmental aspects. *Journal of Industrial Ecology* **10** (1–2), 239–255.

Jung, H., Kappen, J., Hesse, A. & Götz, B. 2011 Wasser- und Abwassersituation in der deutschen Papier- und Zellstoffindustrie – Ergebnisse der Wasserumfrage 2010 (Water and wastewater situation in the German pulp and paper industry – Results of water survey 2010). *Wochenblatt für Papierfabrikation* **139** (9), 337–339.

Kaindl, N. 2011 Mill experience from 6 years of advanced effluent treatment with ozone and biofiltration. In *PTS Environment Symposium 2011* (H.-J. Öller, A. Hutter & S. Bierbaum, eds). PTS, Munich, Germany, 2011, proceedings PTS-WU 1108.

Kersten, A., Hamm, U., Schabel, S. & Öller, H.-J. 2006 Analyse von Papierfabrikationsabwässern vor dem Hintergrund verschärfter EU-Anforderungen (Analysis of paper mill wastewaters against the background of more stringent EU requirements). *IPW – Das Papier*, **60** (6), T79–T88.

Lazarova, V. 2013 Global milestones in water reuse: keys to success and trends in development. *Water21* **15** (4), 12–22.

Mahne, D. 2012 *Combination of constructed wetland and TiO_2 photocatalysis for textile wastewater treatment*. PhD Thesis, University of Nova Gorica, Graduate School, Nova Gorica, Slovenia.

Schmidt, T. & Lange, S. 2000 Treatment of paper mill effluents by the use of ozone and biological systems: large scale application at Lang Papier, Ettringen (Germany). In TAPPI 2000 Environmental Conference & Trade Fair, May 6–10, 2000, Denver.

van der Zee, F. P. & Villaverde, S. 2005 Combined anaerobic-aerobic treatment of azo dyes – A short review of bioreactor studies. *Water Research* **39** (8), 1425–1440.

Visvanathan, C. & Asano, T. 2001 *The Potential for Industrial Wastewater Reuse*. 'Encyclopedia of Life Support Systems', UNESCO Publication, Paris.

First received 21 June 2013; accepted in revised form 25 September 2013. Available online 25 October 2013