

## Review

# Enhancement of biodegradability of industrial wastewaters by chemical oxidation pre-treatment

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**Abstract:** Chemical oxidation technologies are often employed for the treatment of complex industrial effluents that are not amenable to conventional biological methods. The role of chemical oxidation depends on the treatment objectives and may vary from partial remediation to complete mineralization. In the case of partial treatment, chemical oxidation aims at the selective removal of the more bioresistant fractions and their conversion to readily biodegradable intermediates that can subsequently be treated biologically. Coupling chemical pre-oxidation with biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared with the efficiency of each individual stage. This paper reviews recent developments and highlights some important aspects that need to be addressed when considering such integrated schemes.

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**Keywords:** advanced oxidation processes; biodegradation; effluents; pre-treatment; wet oxidation

### NOTATION

AOP	Advanced oxidation process
AOSC	Average oxidation state of carbon
AOX	Adsorbable organic halogen ( $\text{mg dm}^{-3}$ )
$\text{BOD}_{\text{st}}$	Short-time biological oxygen demand ( $\text{g dm}^{-3}$ )
$\text{BOD}_{\text{u}}$	Ultimate biological oxygen demand ( $\text{g dm}^{-3}$ )
$\text{BOD}_x$	Biological oxygen demand after $x$ days ( $\text{g dm}^{-3}$ )
$C$	Concentration of specific substrate ( $\text{g dm}^{-3}$ or $\text{mmol dm}^{-3}$ )
COD	Chemical oxygen demand ( $\text{g dm}^{-3}$ )
$\text{COD}_{\text{partox}}$	Chemical oxygen demand reduction via partial oxidation ( $\text{g dm}^{-3}$ )
DOC	Dissolved organic carbon ( $\text{g dm}^{-3}$ )
DTPA	Diethylenetriaminepentaacetic acid
$\text{EC}_{50}$	Exposure concentration 50
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental protection agency
FBR	Fixed bed reactor
$G_{\text{L}}$	Dilution factor, where the luminescence inhibition is below 20%
IABOD	Immediately available biological oxygen demand ( $\text{g dm}^{-3}$ )
$\text{LC}_{50}$	Lethal concentration 50
MTBE	Methyl tert-butyl ether

MW	Molecular weight ( $\text{kg mol}^{-1}$ )
OME	Olive mill effluent
PAH	Polycyclic Aromatic Hydrocarbons
$P_{\text{O}_2}$	Oxygen partial pressure (MPa)
$P_{\text{tot}}$	Total pressure (MPa)
SBR	Sequencing batch reactor
$T$	Temperature ( $^{\circ}\text{C}$ )
TC	Total carbon ( $\text{g dm}^{-3}$ )
TKN	Total Kjeldahl nitrogen ( $\text{g dm}^{-3}$ )
TOC	Total organic carbon ( $\text{g dm}^{-3}$ )
TP	Total phenols ( $\text{g dm}^{-3}$ )
WAO	Wet air oxidation
$\mu$	Efficiency of COD reduction via partial oxidation

### 1 INTRODUCTION

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfil the above two requirements. However, biological processes do not always give satisfactory results, especially

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applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. Therefore, advanced technologies based on chemical oxidation may be the only viable options for decontaminating a biologically recalcitrant wastewater. Such oxidation technologies are broadly classified as follows:

- (i) advanced oxidation processes (AOPs) including wastewater remediation based on ozone, hydrogen peroxide, hydrogen peroxide/ferrous iron catalyst (the so called Fenton's reagent), UV irradiation, photocatalysis and electrochemical oxidation;
- (ii) wet air oxidation processes (WAO).

The most common AOPs described here can be broadly defined as aqueous phase oxidation methods based primarily on the intermediacy of hydroxyl radicals in the mechanisms leading to the destruction of the target compound, and can be used either separately or in various combinations such as ozone/UV, ozone/hydrogen peroxide, UV/hydrogen peroxide, ozone/UV/hydrogen peroxide.

Sub-critical wet air oxidation refers to the aqueous phase oxidation of organics and oxidizable inorganic components at elevated temperatures (typically between 125 and 300 °C) and pressures (typically between 0.5 and 20 MPa) using a gaseous source of oxygen.<sup>1</sup> Although it has traditionally been employed for the conditioning and treatment of waste activated sludge,<sup>1,2</sup> increasing interest has been shown over the past 10–15 years regarding its use for industrial effluent treatment.

The scope of this paper is to review recently published work in the field of integrated chemical and biological wastewater treatment. Chemical oxidation technologies are evaluated regarding their efficacy to improve the biological treatability of several types of industrial effluents and some key elements of process integration are discussed.

## 2 COUPLING CHEMICAL AND BIOLOGICAL TREATMENT

### 2.1 The concept

Given the specific treatment objectives, the effluent characteristics (eg composition and concentration) and the oxidation potential of the oxidant in question, oxidation technologies may be used either for the complete mineralization of all pollutants to carbon dioxide, water and mineral salts or for the partial removal of certain target pollutants and their conversion to intermediates. In general, a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. A potentially attractive alternative to complete oxidation through chemical means is the use of a chemical oxidation pre-treatment step to convert initially biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water. For instance, organic macromolecules such as soluble polymers may simply be too large to permeate cell walls, which precludes their effective biological oxidation. Chemical oxidation might break these molecules into smaller intermediate compounds (eg short-chain organic acids) that can enter cells and may be more readily biodegradable than the original molecules, since the rate of biological oxidation is generally thought to increase with decreasing molecular size. Conversely, total chemical oxidation of these intermediates to carbon dioxide and water may be difficult and require severe oxidative conditions, since the rate of chemical C–C bond scission seems to decrease with decreasing molecular size. Putting these two separate observations together in a qualitative sense, the concept of an integrated chemical and biological treatment process can be illustrated schematically (see Fig 1). As seen, there appears to be a breakpoint beyond which biological

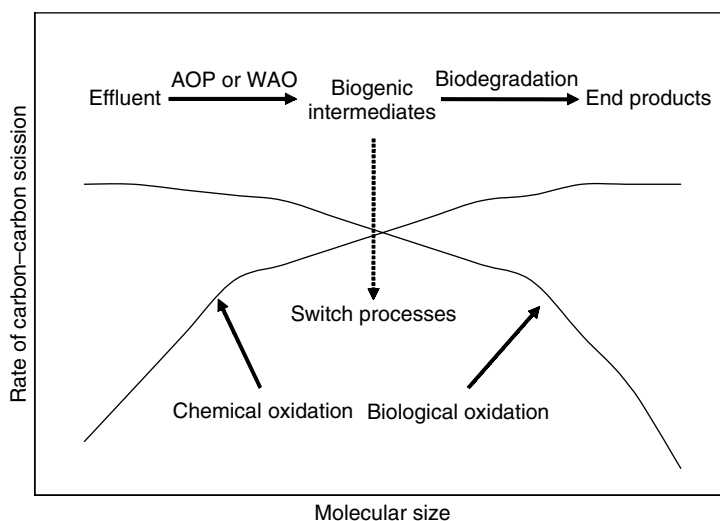


Figure 1. The concept of integrated chemical and biological treatment.

Table 1. Effect of AOP pre-treatment on biological properties (+: positive effect, -: negative effect, 0: insignificant effect, nd: not determined)

Ref	Chemicals degraded/source of effluent	Initial concentration	AOP	Biological degradation	Measure of pre-treatment effect	Effect
4	Mixture of cinnamic, <i>p</i> -coumaric, caffeic and ferulic acids, olive mill effluent (diluted 10 times)	$C = 1 \text{ mmol dm}^{-3}$ (for each acid in the mixture), not explicitly given for olive mill effluent	$\text{O}_3$	Active sludge respirometry	$\text{BOD}_{\text{st}}/\text{COD}$ ratio ( $\text{BOD}_{\text{st}}$ is computed from oxygen uptake rate)	+
5	Human and veterinary antibiotics formulation effluents	$\text{COD} = 0.25\text{--}1.4 \text{ g dm}^{-3}$	$\text{O}_3$ at pH = 3, 7 and 11	Biological oxygen demand	$\text{BOD}_5/\text{COD}$ ratio	+
6	Cork processing effluent	$\text{COD} = 1.9 \pm 0.1 \text{ g dm}^{-3}$ , $\text{BOD}_5 = 1.15 \pm 0.1 \text{ g dm}^{-3}$ , $\text{TP} = 0.29 \pm 0.06 \text{ g dm}^{-3}$	$\text{O}_3$ at pH $\approx 5.4$	Biological oxygen demand, acclimated activated sludge in aerated reactors	$\text{BOD}_5/\text{COD}$ ratio, removal of COD, total phenols and absorbance at 254 nm	+
7	Wine distillery effluent	$\text{COD} = 24.5 \text{ g dm}^{-3}$ , $\text{BOD}_5 \approx 11.2 \text{ g dm}^{-3}$	$\text{O}_3$ at pH $\approx 4$	Acclimated activated sludge in aerated reactors	COD removal	+
8	Industrial effluent with various chlorocarbons, phenols and anilines	$\text{COD} \approx 1.3 \text{ g dm}^{-3}$ , $\text{TOC} \approx 0.5 \text{ g dm}^{-3}$	( $\text{Fe-SiO}_2$ )/ $\text{H}_2\text{O}_2$ /UV light, $\text{Fe}^{3+}$ / $\text{H}_2\text{O}_2$ /UV light	Biological oxygen demand	$\text{BOD}_5/\text{TOC}$ ratio	0/+
9	3-Methylpyridine	$C = 2 \text{ mmol dm}^{-3}$ , $\text{DOC} = 0.15 \text{ g dm}^{-3}$	$\text{O}_3$	Fluidized bed aerated biofilm reactor	DOC removal	nd
10	2,4-Dichlorophenol	$C = 0.1 \text{ g dm}^{-3}$	$\text{O}_3$	Biological oxygen demand, acclimated and non-acclimated activated sludge in aerated reactors	$\text{BOD}_x/\text{COD}$ ratio ( $x = 5, 10, 21$ ), TOC removal	+
11	Phenol, <i>p</i> -chlorophenol, <i>p</i> -bromophenol, <i>p</i> -iodophenol	$C = 1.6 \text{ mmol dm}^{-3}$	Ultrasound at 423 kHz	Enzymatic degradation (horseradish peroxidase with $\text{H}_2\text{O}_2$ )	Substrate removal	+
12	Olive mill effluent	$\text{DOC} = 14.9 \pm 1 \text{ g dm}^{-3}$	Electrochemical oxidation	Incubation with <i>Daphnia magna</i> for 24 h	Toxicity as $\text{LC}_{50}$	0/–
13	2-Nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol (either in mixture or each one alone)	$C = 0.5 \text{ mmol dm}^{-3}$ for each compound in the mixture, $C = 0.4 \text{ mmol dm}^{-3}$ for single solutions	$\text{O}_3$ at pH = 2.5 and 9.5	Biological oxygen demand, incubation for 24 h with <i>Daphnia magna</i>	$\text{BOD}_7/\text{COD}$ ratio, toxicity as $\text{EC}_{50}$	+
14	Sodium pentachlorophenate, paper mill effluents (three streams)	$\text{COD} = 0.16 \text{ g dm}^{-3}$ for NaPCP, $\text{COD} = 2, 3$ and $15 \text{ g dm}^{-3}$ for the three streams	Ultrasound at 500 kHz	Biological oxygen demand, incubation for 5 min with <i>Vibrio fischeri</i>	$\text{BOD}_5$ , $\text{BOD}_5/\text{COD}$ ratio, toxicity as percent inhibition of bioluminescence	0/+

(continued overleaf)

Table 1. Continued

Ref	Chemicals degraded/source of effluent	Initial concentration	AOP	Biological degradation	Measure of pre-treatment effect	Effect
15	Effluents from the manufacturing of whitening agents (three streams)	COD = 1.98; 2.84 and 2.95 g dm <sup>-3</sup> , DOC = 0.49, 0.99 and 0.57 g dm <sup>-3</sup> for the three streams C = 0.1 g dm <sup>-3</sup>	O <sub>3</sub> , O <sub>3</sub> /UV light, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> /UV light, Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV light	Biological oxygen demand, incubation with <i>Vibrio fischeri</i>	COD/BOD <sub>28</sub> ratio, toxicity as G <sub>L</sub> values	-/0/+
16	Procion Red MX-5B, Reactive Brilliant Red K-2G	C = 0.1 g dm <sup>-3</sup>	TiO <sub>2</sub> /UV light	Incubation for 15 min with unspecified bacteria	Toxicity as EC <sub>50</sub>	+
17	Textile mill effluent containing reactive azodyes	DOC ≈ 0.76 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 7.4	Immobilized aerated biomass in rotating disc reactors	DOC and colour removal	+
18	Effluent from semiconductor manufacturing	COD = 62.2 ± 16.8 g dm <sup>-3</sup> (prior to stripping)	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> preceded by air stripping	Non-acclimated activated sludge in SBR	COD removal	nd
19	Green olive fermentation brines (diluted 50% with domestic sewage)	COD ≈ 15.5 g dm <sup>-3</sup> , TOC ≈ 5.1 g dm <sup>-3</sup>	Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub>	Acclimated activated sludge in SBR	COD removal, increase in biomass	+
20	5-Amino-6-methyl-2-benzimidazolone	C ≈ 0.16–0.32 g dm <sup>-3</sup>	Fe <sup>3+</sup> /UV light, Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> /UV light	Immobilized activated sludge (FBR)	DOC removal	+
21	Basic Brown 4, Basic Blue 3	C = 0.02 g dm <sup>-3</sup>	Ultrasound at 520 kHz	Incubation with <i>Vibrio fischeri</i> for 5 min	Relative toxicity index based on EC <sub>50</sub>	+
22	5-Amino-6-methyl-2-benzimidazolone	C = 5 mmol dm <sup>-3</sup>	Electrochemical oxidation	Biological oxygen demand, incubation with <i>Vibrio fischeri</i> , immobilized activated sludge (FBR)	BOD <sub>5</sub> /COD ratio, toxicity as 1/EC <sub>50</sub> , DOC removal	0/+
23	Remazol (Reactive) Black 5	C = 2 g dm <sup>-3</sup>	O <sub>3</sub>	Biological oxygen demand, incubation for 30 min with <i>Vibrio fischeri</i> , Neutral Red cytotoxicity assay	BOD <sub>5</sub> /COD and BOD <sub>28</sub> /COD ratios, toxicity as GL values or percent inhibition to absorbance	-/+
24	Black table olives processing effluents (mixed washing and debittering streams)	COD = 3.31–4.84 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 13	Acclimated activated sludge in batch reactors	COD removal	+
25	Methomyl	C = 0.05 g dm <sup>-3</sup>	TO <sub>2</sub> /sunlight, Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /sunlight	Incubation for 5–30 min with <i>Vibrio fischeri</i> or 24–48 h with <i>Daphnia magna</i> or 72 h with <i>Selenastrum capricornutum</i>	Toxicity as percent inhibition to bacteria	0/+
26	Pentachlorophenol	C ≈ 0.025–0.05 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 5, 7, 10 and 12	Biological oxygen demand, <i>E. coli</i> toxicity test (HACH, 1988–1995b)	BOD <sub>5</sub> /COD ratio, toxicity as percent inhibition to bacteria	+

27	Textile mill effluent (mixture of four process streams)	COD $\approx 9.5 \text{ g dm}^{-3}$	O <sub>3</sub> at pH = 9.7	Acclimated biomass in aerated batch reactors	Respirometric measurements to determine kinetic and stoichiometric constants Toxicity as 100/EC <sub>50</sub>	0
28	Reactive Black 5, Reactive Blue 19, Reactive Blue 21	C = 0.09–34 10 <sup>-3</sup> g dm <sup>-3</sup>	O <sub>3</sub> at pH = 7 and 11	Incubation for 15 min with <i>Vibrio fischeri</i>	Toxicity as 100/EC <sub>50</sub>	-/0/+
29	Reactive Blue 19	C = 0.05 g dm <sup>-3</sup>	TiO <sub>2</sub> /UV light, ZnO/UV light	Incubation for 15 min with <i>Vibrio fischeri</i>	Toxicity as 100/EC <sub>50</sub>	-/+
30	Anthracene, benz[a]pyrene	C = 0.1 g dm <sup>-3</sup>	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> with or without non-ionic surfactants	Bacterial cultures isolated from PAH-contaminated soil	Substrate degradation rates	+
31	Isoproturon	C $\approx 0.04 \text{ g dm}^{-3}$	TiO <sub>2</sub> /UV light	Immobilized activated sludge (FBR), biological oxygen demand, incubation with <i>Vibrio fischeri</i>	DOC removal, BOD <sub>5</sub> /COD ratio, toxicity as 1/EC <sub>50</sub>	+
32	Textile mill effluent	COD = 4 g dm <sup>-3</sup> , DOC = 0.9 g dm <sup>-3</sup>	Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> /UV light	Zahn–Wellens biodegradability test, immobilized activated sludge (FBR)	DOC removal	0
33	Isoproturon, metobromuron, <i>p</i> -nitrotoluene- <i>ortho</i> -sulfonic acid	C = 0.043–1 g dm <sup>-3</sup>	Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> /UV light	Immobilized activated sludge (FBR), biological oxygen demand, incubation with <i>Vibrio fischeri</i>	DOC removal, BOD <sub>5</sub> /COD ratio, toxicity as 1/EC <sub>50</sub>	0/+
34	Aniline, benzoic acid, nitrobenzene, phenol	C = 0.15–0.8 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 4, 7 and 10	Incubation for 15 min with <i>Photobacterium phosphoreum</i>	Toxicity as EC <sub>50</sub>	-/+
35	2-Chlorophenol, 3-chlorophenol, 4-chlorophenol	C = 0.1–0.2 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 7	Incubation for 15 min with <i>Photobacterium phosphoreum</i>	Toxicity as EC <sub>50</sub>	-/+
36	Log yard leachate	COD $\approx 2.5 \text{ g dm}^{-3}$	O <sub>3</sub>	Activated sludge in shake flasks, biological oxygen demand, incubation with <i>Vibrio fischeri</i>	BOD <sub>5</sub> , removal of COD, tannins and lignins, toxicity as EC <sub>50</sub>	0
37	Reactive Black 5	C = 0.5 g dm <sup>-3</sup>	O <sub>3</sub> (uncontrolled pH)	Biological oxygen demand	BOD <sub>5</sub> , BOD <sub>5</sub> /COD and BOD <sub>5</sub> /TOC ratios	+
38	Olive mill effluent	COD = 95 g dm <sup>-3</sup> , BOD <sub>5</sub> = 52 g dm <sup>-3</sup>	O <sub>3</sub> , Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Aerated microorganisms in batch reactors	Removal of COD and total phenols, increase in biomass, Contois rate constants	nd
39	Black table olives washing effluents	COD = 2.7–2.9 g dm <sup>-3</sup> , BOD <sub>5</sub> = 1.56 $\pm$ 0.24 g dm <sup>-3</sup>	O <sub>3</sub>	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
40	Effluents from textile industry (A) and detergent processing (B)	COD $\approx 1.8 \text{ g dm}^{-3}$ (A) and COD = 3.8 g dm <sup>-3</sup> (B)	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> preceded by flocculation	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
41	4-Chlorophenol, 2,4-dichlorophenol	C = 0.3 g dm <sup>-3</sup>	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+

(continued overleaf)

Table 1. Continued

Ref	Chemicals degraded/source of effluent	Initial concentration	AOP	Biological degradation	Measure of pre-treatment effect	Effect
42,43	Mixture of Acid Blue 40 (dyestuff), Tetrapol CLB (softener) and Avivaz KG concentrate (detergent)	COD $\approx 2.2 \text{ g dm}^{-3}$ , DOC $\approx 0.4 \text{ g dm}^{-3}$	O <sub>3</sub> , H <sub>2</sub> O <sub>2</sub> , UV light, H <sub>2</sub> O <sub>2</sub> /UV light, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> /UV light, O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /UV light	Acclimated and non-acclimated activated sludge in shake flasks, dehydrogenase activity assay	Monod rate constants, enzyme activity, percent inhibition to microbial growth	+
44	Aquaculture effluent	COD $\approx 8.7 \pm 14\% \text{ g dm}^{-3}$ , BOD $\approx 1.7 \pm 30\% \text{ g dm}^{-3}$	Ultrasound at 50 kHz	Psychrophilic anaerobic digestion (18–22 °C)	Removal of COD and phosphorus, biogas production rate	+
45	Olive mill effluent (diluted 10 times with domestic sewage)	COD $\approx 14.7 \text{ g dm}^{-3}$ , TOC $\approx 4.9 \text{ g dm}^{-3}$	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Biological oxygen demand	BOD <sub>U</sub> /COD ratio	-/+
46	Amino-6-methyl-2-benzimidazolone	COD $\approx 6.4 \text{ g dm}^{-3}$	Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> /UV light	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
47	Chlorobenzene, 2,4-dichlorophenol	C $\approx 0.075\text{--}0.15 \text{ g dm}^{-3}$	Ultrasound at 360 or 618 kHz	Activated sludge	COD removal, oxygen uptake	+
48	n-Methyl-p-aminophenol (metol)	C = 1–6 mmol dm <sup>-3</sup>	O <sub>3</sub> at pH = 3, 5 and 7	Incubation with <i>Selenastrum capricornutum</i> or <i>Ankistrodesmus braunii</i>	Inhibition to algal growth	+
49,50	Wine distillery effluent (diluted 10 times with domestic sewage)	COD $\approx 2.3 \text{ g dm}^{-3}$	O <sub>3</sub>	Acclimated activated sludge	Removal of COD, TOC, TKN, total phenols and UV <sub>254</sub> absorbance, Contois rate constants	+
51	Black table olives washing effluents	COD $\approx 6 \text{ g dm}^{-3}$ , BOD <sub>5</sub> $\approx 5 \text{ g dm}^{-3}$	O <sub>3</sub> at pH = 4, 6.5 and 9	Acclimated activated sludge in batch reactors	Removal of COD and total phenols, Contois rate constants	+
52	Pentachlorophenol	C = $26.7 \cdot 10^{-3} \text{ g dm}^{-3}$	Ultrasound at 200 kHz	Incubation with <i>Salmonella typhimurium</i> strains TA98 and TA100	Increase in biomass	+
53,54	Pyrene, benzo[a]pyrene	Not explicitly given	Ozonated water is fed to a column reactor packed with glass beads and 1 g pyrene or 0.15 g benzo[a]pyrene	Biological oxygen demand, <i>E. coli</i> toxicity test (HACH, 1988–1995b)	BOD <sub>x</sub> (x = 5, 10, 15, 20), degradation of substrate and intermediates, COD removal, toxicity as percent inhibition to bacteria	nd
55	Dyestuff processing effluent (two streams)	COD = $9.2 \text{ g dm}^{-3}$ (stream A) and COD = $73 \text{ g dm}^{-3}$ (stream B)	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Acclimated activated sludge (FBR), biological oxygen demand	COD removal, BOD <sub>5</sub> /COD ratio	+

56	Wine distillery effluent (diluted 0–20 times with domestic sewage)	COD $\approx$ 1.3–21.7 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 5.4, 7 and 10	Biological oxygen demand	BOD/COD ratio	-/+
57	Olive mill effluent (diluted about 3 times with distilled water)	COD $\approx$ 34 g dm <sup>-3</sup>	O <sub>3</sub>	Acclimated activated sludge in batch reactors	COD removal, Grau kinetic constants	+
58	Reactive Yellow KD <sup>-</sup> 3G, Reactive Red 15, Reactive Red 24, Cationic Blue X-GRL, Methyl Orange, wool textile effluent	C = 0.1 g dm <sup>-3</sup> for model solutions of azo dyes or COD $\approx$ 0.12 g dm <sup>-3</sup> for the effluent	TiO <sub>2</sub> /UV light	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
59	Textile mill effluent (mixed streams from acrylic fibre and yarn dyeing)	COD = 1.9 g dm <sup>-3</sup>	Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub>	Accumulated biomass in aerated batch reactors	Respirometric measurements to determine kinetic and stoichiometric constants	+
60	Sodium pentachlorophenate	C $\approx$ 0.03 g dm <sup>-3</sup>	Ultrasound at 500 kHz	Incubation for 5 min with <i>Vibrio fischeri</i> or 24 h with <i>Daphnia magna</i> or 28 days with activated sludge	Toxicity as percent inhibition of bioluminescence or 1/EC <sub>50</sub>	+
61	Paper mill effluents (two streams)	COD $\approx$ 0.4 g dm <sup>-3</sup> (either stream) TOC = 0.19 g dm <sup>-3</sup>	O <sub>3</sub>	Biofiltration	COD removal	+
62	Mixture of vanillin (8 mg dm <sup>-3</sup> ), glyoxal (3 mg dm <sup>-3</sup> ), sodium formate (500 mg dm <sup>-3</sup> ), sodium acetate (100 mg dm <sup>-3</sup> ) and EDTA or DTPA (107 mg dm <sup>-3</sup> ) in the form of iron complexes		O <sub>3</sub> /UV light at pH = 7	Activated sludge culture	COD removal, increase in biomass	+
63	Bleaching effluents from wood processing (two streams)	COD $\approx$ 1.6 g dm <sup>-3</sup> , AOX = 7.7 mg dm <sup>-3</sup> (stream A) and COD $\approx$ 2.3 g dm <sup>-3</sup> , AOX = 73 mg dm <sup>-3</sup> (stream B)	TiO <sub>2</sub> /UV light/O <sub>2</sub> , ZnO/UV light/O <sub>2</sub>	Accumulated activated sludge culture, biological oxygen demand, incubation for 5–15 min with <i>Photobacterium phosphoreum</i>	COD removal, BOD <sub>5</sub> /COD ratio, increase in biomass, toxicity as 100/EC <sub>50</sub>	+
64	Olive mill effluent	COD = 121.8 g dm <sup>-3</sup> , TC = 34.2 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 8	Anaerobic digestion of diluted samples with mixed acclimated and non-acclimated sludge	Methane and volatile fatty acids production yields	-
65	Effluent from 4,4'-diaminostilbene-2,2'-disulfonic (DSD) acid manufacturing	COD = 21.9 g dm <sup>-3</sup> , TOC $\approx$ 4.8 g dm <sup>-3</sup>	O <sub>3</sub> at pH = 2.5, Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub>	Biological oxygen demand, Warburg respirometry	BOD <sub>5</sub> /COD ratio, oxygen uptake	+

(continued overleaf)

Table 1. Continued

Ref	Chemicals degraded/source of effluent	Initial concentration	AOP	Biological degradation	Measure of pre-treatment effect	Effect
66	<i>p</i> -Nitrotoluene- <i>ortho</i> -sulfonic acid	$C \approx 1 \text{ g dm}^{-3}$ , TOC $\approx 0.4 \text{ g dm}^{-3}$	$\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ light	Immobilized acclimated activated sludge (FBR), biological oxygen demand, Zahn–Wellens biodegradability test, incubation with <i>Photobacterium phosphoreum</i>	$\text{BOD}_5/\text{TOC}$ and $\text{BOD}_5/\text{COD}$ ( $x = 1, 2, 3, 4, 5$ ) ratios, TOC removal, toxicity as $1/\text{EC}_{50}$	+
67	Olive mill effluent (50% diluted with water)	$\text{COD} = 59.9 \text{ g dm}^{-3}$	$\text{O}_3$	Anaerobic digestion with immobilized acclimated biomass	Methane production yield	+
68	Mixture of acrylonitrile and styrene	Not explicitly given	$\text{O}_3$	Acclimated activated sludge	COD removal	+
69	Lignin, tannic acid, chlorotetracycline, EDTA	$\text{COD} = 2.5 \pm 0.2 \text{ g dm}^{-3}$	Electrochemical oxidation	Incubation for 5–15 min with <i>Photobacterium phosphoreum</i>	Toxicity as $\text{EC}_{50}$	+
70,71	Biologically pre-treated tan-yard and beamhouse effluents	$\text{COD} \approx 0.5 \text{ g dm}^{-3}$ for tan-yard and $\text{COD} \approx 0.1 \text{ g dm}^{-3}$ for beamhouse	$\text{O}_3$ at pH = 7	Aerated biomass in fixed bed column, EN ISO 9888 biodegradability test, EN ISO 9509 nitrification test, incubation with <i>Vibrio fischeri</i>	Removal of COD, DOC and ammonia, toxicity as percent inhibition of bioluminescence or $1/\text{EC}_{20}$	+
72	Orange II	$C = 0.5 \text{ g dm}^{-3}$	$\text{O}_3$ at pH = 7	Biological oxygen demand	COD removal, $\text{BOD}_5$	+
73	2,4-Dichlorophenoxy acetic acid, propoxur	$C = 50 \text{ mg dm}^{-3}$	$\text{TiO}_2/\text{UV}$ light/ $\text{O}_2$	Incubation for 15 min with <i>Photobacterium phosphoreum</i>	Toxicity as percent inhibition of bioluminescence	–
74	3-Methylpyridine, 5-ethyl-2-methylpyridine	$C = 2 \text{ mmol dm}^{-3}$	$\text{O}_3$ at pH = 7	Mixed cultures in fluidized biofilm reactor	Removal of DOC and substrate	nd
75	Dispersal Yellow C-4R, Dispersal Scarlet B-RN, Cibacron Red FB, Solophenyl Orange T4RL	$\text{COD} \approx 60\text{--}250 \text{ mg dm}^{-3}$	$\text{TiO}_2/\text{UV}$ light/ $\text{O}_2$	Biological oxygen demand	$\text{BOD}/\text{COD}$ ratio	+
76	Textile mill effluent	$\text{COD} \approx 0.7 \text{ g dm}^{-3}$	Electrochemical oxidation preceded by coagulation	Activated sludge	Removal of COD and turbidity	+
77	Chlorendic acid	$C = 0.5 \text{ g dm}^{-3}$	$\text{O}_3$ , UV light, $\text{O}_3/\text{UV}$ light (all at pH $\approx 7$ )	Acclimated biomass in aerated batch reactors	DOC removal, Monod rate constants	+



Table 2. Effect of WAO pre-treatment on biological properties (+: positive effect, -: negative effect, 0: insignificant effect)

Ref	Chemicals degraded/ source of effluent	Initial concentration	WAO conditions	Biological degradation	Measure of pre- treatment effect	Effect
78	Kraft-pulp bleaching effluents (two streams)	COD = 2.9 and 3.6 g dm <sup>-3</sup> , AOX = 24.1 and 19.6 mg dm <sup>-3</sup> for the two streams	$P_{\text{tot}} = 5.5 \text{ MPa}$ , $T = 190 \text{ }^\circ\text{C}$ , trickle bed and batch recycle reactors with TiO <sub>2</sub> or Ru/TiO <sub>2</sub>	Incubation with <i>Daphnia magna</i> for 48 h and <i>Vibrio fischeri</i> for 30 min, Zahn-Wellens biodegradability test	Toxicity as EC <sub>50</sub> , COD removal	-/+
79	Morphine processing effluent	COD = 26.7 g dm <sup>-3</sup>	$P_{\text{tot}} = 0.65\text{--}0.8 \text{ MPa}$ , $T = 140\text{--}160 \text{ }^\circ\text{C}$ , treatment time = 2 h, batch bubble reactor, with or without Cu <sup>2+</sup> , Co <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Mn <sup>2+</sup> homogeneous catalysts	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
80	2,4-Dichlorophenol	C = 0.2 g dm <sup>-3</sup>	$P_{\text{O}_2} = 1 \text{ MPa}$ , $T = 125\text{--}160 \text{ }^\circ\text{C}$ , upflow fixed bed reactor, with or without Mn/Ce heterogeneous catalyst	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
81	Sodium dodecylbenzene sulfonate (SDBS)	C = 1.6 g dm <sup>-3</sup> , COD $\approx 3 \text{ g dm}^{-3}$ , TOC $\approx 0.8 \text{ g dm}^{-3}$	$P_{\text{O}_2} = 1.5 \text{ MPa}$ , $T = 180\text{--}240 \text{ }^\circ\text{C}$ , treatment time = 2 h, semibatch stirred reactor, with or without H <sub>3</sub> PO <sub>4</sub> (acid catalysis)	Shake flasks (10 days) with biomass acclimated to SDBS and intermediates	Removal of COD and TOC, degradation of SDBS and intermediates	+
82	Lignin	C $\approx 0.3 \text{ g dm}^{-3}$	$P_{\text{O}_2} = 0.4\text{--}1.5 \text{ MPa}$ , $T = 110\text{--}165 \text{ }^\circ\text{C}$ , treatment time = 2 h, batch stirred reactor, with NaOH	Biological oxygen demand	BOD/COD and IABOD/BOD ratios	+
83	Pulp and paper mill effluent	COD = 6–8 g dm <sup>-3</sup> , TOC = 1.2–1.9 g dm <sup>-3</sup>	$P_{\text{O}_2} = 0.5\text{--}1.5 \text{ MPa}$ , $T = 170\text{--}200 \text{ }^\circ\text{C}$ , treatment time = 2 h, batch stirred reactor	Biological oxygen demand	BOD/COD and IABOD/COD ratios	+
84	1-Amino-8-naphthol-3,6-disulfonic acid (H-acid)	C = 10 g dm <sup>-3</sup>	$P_{\text{O}_2} = 3 \text{ MPa}$ , $T = 200 \text{ }^\circ\text{C}$ , treatment time = 2 h, batch stirred reactor, with Cu/Ce heterogeneous catalyst	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	+
85	Linear alkylbenzene sulfonate (LAS)	C = 1 g dm <sup>-3</sup> , COD $\approx 2.7 \text{ g dm}^{-3}$ , TOC $\approx 0.7 \text{ g dm}^{-3}$	$P_{\text{O}_2} = 1.3 \text{ MPa}$ , $T = 200 \text{ }^\circ\text{C}$ , treatment time = 6.5 h, semibatch or continuous stirred reactor	Enrichment bioreactors, biological oxygen demand with acclimated biomass	Removal of COD, TOC and active detergency, BOD <sub>5</sub> /COD and BOD <sub>5</sub> /TOC ratios	-
86	Green table olives processing effluent	COD = 12–14.7 g dm <sup>-3</sup> , TOC $\approx 3.3\text{--}3.9 \text{ g dm}^{-3}$	$P_{\text{tot}} = 3\text{--}7 \text{ MPa}$ , $T = 170\text{--}210 \text{ }^\circ\text{C}$ , treatment time = 6 h, batch stirred reactor, with or without Cu <sup>2+</sup> homogeneous catalyst or H <sub>2</sub> O <sub>2</sub> promoter	Acclimated activated sludge in batch reactors at 20 °C	Removal of COD and TOC, BOD <sub>5</sub> , increase in biomass, maximum specific growth rate	-/+

(continued overleaf)

Table 2. Continued

Ref	Chemicals degraded/ source of effluent	Initial concentration	WAO conditions	Biological degradation	Measure of pre- treatment effect	Effect
87	Olive mill effluent (diluted 10 times with domestic sewage)	COD $\approx$ 14.7 g dm <sup>-3</sup> , TOC $\approx$ 4.9 g dm <sup>-3</sup>	$P_{\text{tot}}$ = 7 MPa, $T$ = 180 °C, treatment time = 6 h, batch stirred reactor, with or without CuO/C, Pt/Al <sub>2</sub> O <sub>3</sub> heterogeneous catalysts or H <sub>2</sub> O <sub>2</sub> promoter $P_{\text{O}_2}$ = 2.1 MPa, $T$ = 200 °C, treatment time = 4 h, batch stirred reactor	Biological oxygen demand	BOD <sub>5</sub> /COD ratio as a function of COD removal efficiency via partial oxidation, BOD rate constant ultimate	0/+
88	Polyvinyl alcohol	$C$ = 5 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 2.1 MPa, $T$ = 200 °C, treatment time = 4 h, batch stirred reactor	Biological oxygen demand	BOD <sub>5</sub> , BOD <sub>6</sub> /COD ratio	+
89,90	Polyethylene glycol (MW = 10 000)	$C$ = 1 g dm <sup>-3</sup> , TOC = 0.55 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 3 MPa, $T$ = 100–150 °C, continuous stirred reactor with or without nanofiltration and recycle of retentate	Acclimated biomass in continuous aerobic reactors at 35 °C	TOC removal	+
91	Pulp and paper mill effluent (two streams)	COD = 10–19 g dm <sup>-3</sup> for stream A and COD = 6.5–7.3 g dm <sup>-3</sup> for stream B	$P_{\text{O}_2}$ = 1 MPa, $T$ = 130–200 °C, treatment time = 2 h, batch stirred reactor, with or without catalysts (Cu/Co/Bi, Co/Bi, Fe/Mn on various supports, Cu <sup>2+</sup> )	Biological oxygen demand	BOD/COD ratio	+
92	Eight amides (formamide, acetamide, <i>n</i> -butyramide and alkylated substitutes) and 11 polymers (polyethylene glycols with MW = 200–20 000, polyvinyl alcohol, polypropylene glycol, polyacryl amide, polyacrylic acid)	$C$ = 5 g dm <sup>-3</sup> for amides, TOC = 2.5 g dm <sup>-3</sup> for polymers	$P_{\text{O}_2}$ = 3 MPa, $T$ = 235–275 °C, treatment time = 2 h for amides and $P_{\text{O}_2}$ = 1.96 MPa, $T$ = 220 °C, treatment time = 2 h for polymers	Biological oxygen demand	BOD/COD ratio	+
93	<i>p</i> -Coumaric acid	$C$ = 0.75 g dm <sup>-3</sup> , COD $\approx$ 1.3 g dm <sup>-3</sup> , TOC $\approx$ 0.5 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 3 MPa, $T$ = 133–155 °C, treatment time = 1.5 h, semibatch stirred reactor	Biochemical methane potential assay	DOC removal	–
94,95	Orange II	$C$ = 0.5 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 1 MPa, $T$ = 180–240 °C, treatment time = 2 h, semibatch stirred reactor, with or without CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	0/+
96	Quinoline	$C$ = 0.25 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 0.4–2 MPa, $T$ = 260–280 °C, treatment time = 1 h, batch stirred reactor	Inhibition test of <i>Nitrosomonas</i> and <i>Nitrobacter</i>	Nitrification rates compared with controls to determine inhibition	–
97	Polyethylene glycols (MW = 62, 150, 600, 1 000, 10 000, 35 000)	TOC = 0.55 g dm <sup>-3</sup>	$P_{\text{O}_2}$ = 2–3 MPa, $T$ = 110–240 °C, treatment time = 2 h, semibatch stirred reactor	Biological oxygen demand	BOD <sub>5</sub> /COD ratio	0/+

treatment becomes more attractive than chemical oxidation in terms of rate.

## 2.2 Recent studies and general trends

A great deal of research into chemical oxidation pre-treatment has been undertaken over the past 20–25 years and the more recent articles (eg those published since 1996) dealing with the use of AOPs and WAO as the pre-treatment stage are summarized in Tables 1 and 2 respectively. It should be pointed out that the last column in these tables qualitatively shows the impact of the integrated process on the effectiveness of the overall system compared with controls (eg direct biological treatment without chemical pre-oxidation). Articles published prior to 1996 are reviewed elsewhere<sup>3</sup> and are not included in this work. Nonetheless, a comparison between recent and earlier studies is attempted in Fig 2 which shows the relative distribution of various AOPs and WAO used for pre-treatment.

From the data shown in Tables 1 and 2 and Fig 2, several generic points to be discussed are drawn and can be summarized as follows:

- (i) several different pre-treatments have been employed with emphasis given on AOPs; of these, ozonation (alone or in conjunction with another oxidant) appears to be the most popular pre-treatment;
- (ii) there appears to be an increasing interest on the application of WAO;
- (iii) studies cover a broad spectrum of industry-related pollutants ranging from single-component model solutions to multi-component solutions to actual effluents;
- (iv) the effect of pre-treatment on biological properties is usually evaluated by means of simple biodegradability and toxicity tests; relatively fewer studies report biological degradation experiments as part of an integrated chemical and biological process.

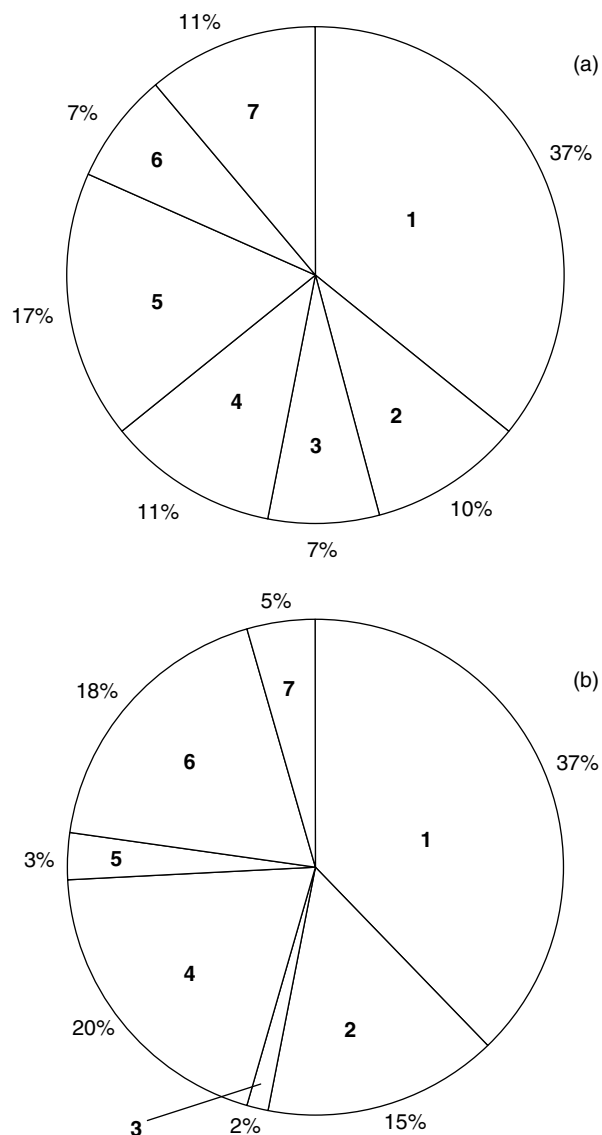
## 3 TREATMENT SCHEMES

### 3.1 Chemical pre-treatment

#### 3.1.1 Chemical pre-treatment by means of AOPs

Chemical pre-treatment should ideally be highly selective towards the least biodegradable fractions of wastewaters, thus leaving the most biodegradable species intact for the subsequent biological step. Unfortunately, the dominant mechanism through which the majority of AOPs and WAO degrade organic pollutants is the formation of hydroxyl radicals that are highly reactive but poorly selective.

Ozone has many of the oxidizing properties desirable for use in wastewater treatment, although it has been traditionally employed in water treatment. Unlike other oxidants, there are two mechanisms through which ozone can degrade organic pollutants, namely: (i) direct electrophilic attack and (ii) indirect attack



**Figure 2.** Distribution of chemical oxidation technologies used for pre-treatment: (a) this work, (b) data from Ref 3. 1, Ozonation; 2, Fenton; 3, photo-Fenton; 4, photolysis/photocatalysis; 5, WAO; 6, combination of various AOPs (eg  $O_3/UV$ ,  $O_3/H_2O_2$  etc); 7, other processes (eg electrochemical oxidation, ultrasound,  $\gamma$ -ray irradiation).

through the formation of hydroxyl radicals. Direct attack by molecular ozone (commonly known as ozonolysis) occurs at acidic or neutral conditions and is a selective reaction resulting in the formation of carboxylic acids as end-products that cannot be oxidized further by molecular ozone. Compounds susceptible to ozonolysis are those containing C=C double bonds, specific functional groups (eg OH,  $CH_3$ ,  $OCH_3$ ) and atoms carrying negative charge (N, P, O, S).<sup>98</sup> This unique feature renders ozonation an attractive pre-treatment for certain classes of effluents. For instance, agro-industrial effluents such as olive mill wastewaters typically contain readily biodegradable fractions such as proteins and sugars and bioresistant fractions such as polyphenols and unsaturated acids. In the context of chemical pre-treatment, ozonation would ideally leave the former intact, while attacking

preferentially the double bonds of the latter. At high pH values, ozone decomposes to non-selective hydroxyl radicals which, in turn, attack the organic pollutants. Therefore, the pH of the effluent is a major factor determining the efficiency of ozonation pre-treatment since it can alter degradation pathways (and consequently the distribution of intermediates formed) as well as kinetics. Ozonation is usually coupled with another oxidant such as hydrogen peroxide or UV irradiation to enhance the formation of hydroxyl radicals in aqueous phase.

Photocatalysis has long been used for partial or complete wastewater remediation and numerous studies on the subject are being published each year. In the context of integrated treatment, two schemes have been given particular attention, namely: (i) homogeneous photo-Fenton processes and (ii) heterogeneous semiconductor processes.

A major shortcoming of all catalytic treatments based on homogeneous catalysts is the need to remove and/or recover the catalyst from the treated effluent prior to subsequent biological treatment or disposal. This usually requires an additional treatment step such as precipitation and filtration. Bozzi *et al*<sup>8</sup> have recently developed a new photo-Fenton catalyst consisting of iron ions immobilized on silica fabrics. The catalyst was capable of enhancing the biodegradability of an industrial effluent containing various chlorocarbons, phenols and anilines as indicated by an increase of the BOD<sub>5</sub>/TOC ratio of the original effluent. More importantly, the catalyst exhibited considerable long-term stability without loss of activity for several consecutive cycles of operation. Conversely, the respective homogeneous photo-Fenton process had practically no effect on the biodegradability of the effluent.

Semi-conductor photocatalysis involves the use of a light-requiring solid catalyst which is continuously photoactivated and thereby serves as a source of active centres on the catalyst surface capable of either interacting directly with the adsorbed organics, or stimulating the formation of hydroxyl radicals. Of the various photocatalysts tested in wastewater treatment, TiO<sub>2</sub> is by far the most popular one, while others such as CdS and ZnO have received less attention.<sup>99</sup> Yeber *et al*<sup>63</sup> compared the activity of TiO<sub>2</sub> and ZnO with respect to the effect of photocatalytic pre-treatment on the biological properties of a pulp mill bleaching effluent. In further studies, Lizama *et al*<sup>29</sup> studied the TiO<sub>2</sub> and ZnO photocatalytic treatment of a textile anthraquinone dye and found that ZnO was more active than TiO<sub>2</sub> with respect to dye and TOC removal. With either catalyst, acute toxicity to *Vibrio fischeri* increased sharply during the early stages of the pre-treatment presumably due to the formation and accumulation of toxic intermediates and progressively decreased as intermediates were further degraded.

In recent years, there has been increasing interest in the use of electrochemical methods for wastewater treatment. Organics can be destroyed by direct anodic

oxidation or a combination of direct and indirect oxidation; the latter occurs if chlorides are present in the effluent and involves the *in-situ* generation of powerful oxidants such as chlorine, hydroxyl radicals and oxygen.<sup>100</sup>

Although materials such as graphite, PbO<sub>2</sub> and SnO<sub>2</sub> have been employed as the anode, titanium electrodes covered by thin layers of various noble metals (eg platinum, iridium, rhodium, ruthenium) are widely used due to increased stability, durability and efficiency.<sup>22,100</sup> Electrochemical oxidation, a relatively easy to operate process which does not require the use of extra oxidants or other chemicals, has been recently tested with respect to its applicability as chemical pre-treatment for industrial effluents.<sup>12,22,76</sup>

A relatively innovative process that deserves particular attention is based on the use of ultrasound (typically in the range 20–1000 kHz) for the treatment of chemical contaminants in water. Ultrasonic irradiation of aqueous solutions induces acoustic cavitation, which can be defined as the cyclic formation, growth and subsequent collapse of micro-bubbles or cavities occurring in extremely small intervals of time and releasing large quantities of energy over a small location. Thus, cavitation serves as a means of concentrating the diffused energy of ultrasound into micro-reactors. The heat from the cavity implosion decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals, which may recombine during the cooling phase to form hydrogen peroxide and molecular hydrogen.<sup>101</sup> Sonochemical degradation in aqueous phase involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble–liquid interface and hydroxyl radical-mediated reactions at the bubble–liquid interface and/or in the liquid bulk.<sup>102</sup> The relative importance of the various mechanisms involved primarily depends on the physicochemical properties of the pollutants in question; the process is more selective towards hydrophobic and volatile species that can be degraded easily via pyrolytic reactions, while hydrophilic and less volatile compounds are degraded slowly via hydroxyl radical-induced reactions. Various investigations report successful removal of a wide range of organic pollutants from relatively dilute aqueous solution and it appears that the applications of this novel means of reaction in environmental remediation and pollution prevention is unlimited.<sup>103</sup> Few recent studies<sup>11,14,21,44,47,60</sup> have explored the possibility of employing ultrasonic irradiation as chemical pre-treatment.

### 3.1.2 Chemical pre-treatment by means of WAO

WAO is ideally suited to effluents that are either too dilute to incinerate or too toxic and/or concentrated for biological treatment. At the conditions typically employed in sub-critical WAO conditions, COD reductions are usually between 75 and 90%, thus implying that complete mineralization cannot be achieved.<sup>104</sup> This is so since wet air oxidation of organic compounds proceeds through the formation

of lower MW compounds which are recalcitrant to chemical oxidation and tend to accumulate in the liquid phase. Such compounds typically include oxygenated short-chain organic acids (such as acetic acid) whose further chemical oxidation to CO<sub>2</sub> and water is usually the rate limiting step in most oxidation processes; moreover, organic nitrogen may easily be converted to ammonia which is also very stable in oxidation conditions. Nonetheless, when the temperature and pressure are raised above the critical point of water (374 °C, 22.1 MPa), extremely high removal rates can be achieved (>99% within few minutes) even for the most refractory pollutants; this process is known as super-critical wet air oxidation.

Sub-critical WAO has gained a lot of attention as a promising pre-treatment over the past decade. Its main advantage over other technologies is that operating conditions can easily be modified to achieve partial or near-complete treatment of moderately or highly concentrated effluents (10–100 g dm<sup>-3</sup> of COD). Moreover, the process becomes thermally self-sustained at >20 g dm<sup>-3</sup> of feed COD and creates minimum air pollution since the gas phase mainly consists of spent oxygen and CO<sub>2</sub>.

Nonetheless, wet air oxidation is still an expensive process to install and operate because of the severe conditions required. High capital and operating costs are associated with the elevated pressures and temperatures employed, long residence times and use of construction materials which should be resistant to the high corrosion rates occurring under severe operating conditions. In this light, costs can be significantly reduced by the use of suitable homogeneous (eg copper and iron salts) or heterogeneous (eg noble metals such as Pt, Pd, Ru, Rh and transition metal oxides such as Cu, Fe, Co, Mn, Ni, Sn oxides in various combinations) catalysts capable of promoting reactions under milder operating conditions and shorter residence times.

Another potential advantage of catalytic wet air oxidation over the uncatalysed oxidation is that, in the context of an integrated chemical and biological treatment process, the use of a suitable catalyst might alter the selectivity of the uncatalysed oxidation towards the most readily biodegradable intermediates. This has been demonstrated in a recent study<sup>79</sup> where both the BOD<sub>5</sub> content and the BOD<sub>5</sub>/COD ratio of a pharmaceutical effluent subject to homogeneously catalysed WAO were substantially greater than the respective values of the uncatalysed process, while COD removal was practically common

for both catalysed and uncatalysed runs. Similar findings have been reported by Lee *et al*<sup>80</sup> who found that wet air oxidation of 2,4-dichlorophenol over an Mn/Ce catalyst led to the formation of intermediates that were more biodegradable (as assessed by the BOD<sub>5</sub>/COD ratio) than those formed during the uncatalysed reaction. WAO of azo dye Orange II over a CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst led to greater improvements of biodegradability (as assessed by the BOD<sub>5</sub>/COD ratio) than the corresponding uncatalysed process.<sup>94,95</sup> However, this was attributed to the smaller concentrations of intermediates formed during the catalytic process (eg greater COD removal) rather than to differences in product distribution since both catalytic and uncatalysed processes proceeded through the formation of common intermediates.

### 3.2 Chemical pre-treatment coupling oxidation and separation

To improve treatment efficiency, chemical oxidation may be coupled with a filtration step prior to biological treatment, as illustrated in Fig 3. The rationale behind this is that the partially oxidized effluent is passed over a membrane module, where larger (and less biodegradable) molecules are recycled into the chemical oxidation reactor, while the permeate containing the smaller (and potentially more biodegradable) compounds is fed to the biological treatment. In this respect, process efficiency increases since membrane selectively retains large molecules to undergo further chemical oxidation. This approach was demonstrated in a study regarding treatment of a polymer-containing effluent in a continuous sequence comprising uncatalysed WAO and nanofiltration.<sup>105</sup> This sequence was further coupled with aerobic biodegradation post-treatment and was capable of reducing the TOC content of the effluent by about 95% at a biological residence time of 6 h; conversely, an integrated process comprising WAO and aerobic degradation alone would require a biological residence time of 48 h to achieve 95% mineralization. Direct biological treatment (without any pre-treatment) of the effluent at a biological residence time of 48 h resulted in only about 35 ± 13% removal.<sup>89</sup>

Another pre-treatment combining separation and chemical oxidation was proposed by Lin and Kiang<sup>18</sup> who treated a complex, strong effluent from a semiconductor-processing plant by means of sequential air stripping, Fenton oxidation and aerobic degradation. Air stripping was found capable of removing most of the volatile organics originally present in the effluent,

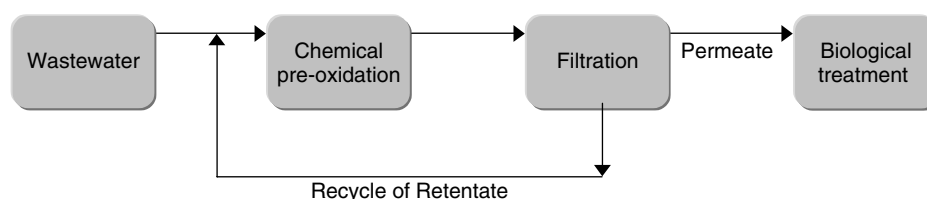


Figure 3. Coupling chemical, physical and biological treatment.

thus reducing the initial COD by as much as about 35%; the remaining organics were first diluted with other low-strength effluents from the same plant and then treated by Fenton oxidation operating at 70 °C followed by biological post-treatment in a sequencing batch reactor. With this treatment train, the inlet COD which was as high as 80 g dm<sup>-3</sup> was reduced to values below 0.1 g dm<sup>-3</sup>.

### 3.3 Other treatment schemes

Other types of integrated treatment in which a preceding biological step is followed by further chemical oxidation (eg biological → chemical → biological or biological → chemical) have also been reported in the literature. Such integrated systems may be favourable for wastewaters that initially contain some biodegradable fractions which could be easily removed first, and so subsequently would not compete for the chemical oxidant. Libra and Sosath<sup>17</sup> studied two schemes to treat textile effluents, namely: (i) ozonation followed by aerobic degradation and (ii) two-stage anaerobic–aerobic pre-treatment followed by ozonation and subsequent aerobic degradation. Biological pre-treatment reduced colour by about 70% although the organic content of the effluent remained practically unchanged. In both treatment schemes, mineralization was achieved in the ozonation–aerobic degradation stage.

In further studies, the treatment of cork-processing<sup>6</sup> and olive mill<sup>57</sup> effluents by means of sequential aerobic degradation–ozonation and ozonation–aerobic degradation was investigated. COD removal during biological pre-treatment was 27% and 73.6% for cork-processing and olive mill effluents respectively, thus implying that most of the biodegradable fractions were removed first biologically. Overall COD removals of 77% and 65% respectively were achieved for the aerobic degradation–ozonation and ozonation–aerobic degradation schemes of cork-processing effluent; the respective values for the olive mill effluent were 81.8% and 84.6%.

## 4 TREATMENT OF INDUSTRIAL EFFLUENTS

### 4.1 Agro-industrial effluents

#### 4.1.1 Olive oil mill effluents

Olive oil production is one of the most important agricultural industries in the Mediterranean area and is of fundamental economic importance to several countries. Mediterranean countries produce as much as 95% of the worldwide production which is about 2.5 × 10<sup>6</sup> tons, 70% of which is shared between Spain, Italy and Greece.<sup>106</sup> Olive oil mills vegetation and washing effluents (OME) are amongst the strongest industrial effluents with an annual production rate of more than 3 × 10<sup>7</sup> m<sup>3</sup> and may have COD values as high as about 220 g dm<sup>-3</sup> with the organic matter mainly consisting of polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids and oil.<sup>107</sup>

The strength of OME as well as the presence of high concentrations of polyphenolic compounds (up to about 10 g dm<sup>-3</sup>) which are difficult to biodegrade due to their bactericide and antioxidant properties render OME inappropriate for biological treatment by conventional methods. Moreover, the seasonal character of olive oil production (which typically lasts between December and February) in small plants distributed over large areas as well as the stringent discharge levels for this type of waste (eg COD < 0.2 g dm<sup>-3</sup> in Spain<sup>108</sup>) would require a flexible, decentralized unit to treat OME effectively.

In this respect, several oxidation technologies have been tested either alone or in conjunction with a biological stage for the treatment of OME. Benitez *et al*<sup>57</sup> reported that ozonation of dilute OME (with COD varying between 10 and 34 g dm<sup>-3</sup>) for 8 h at temperatures between 10 and 40 °C and pH values between 5 and 9 resulted in a moderate COD reduction (between 12% and 28%). This was, however, accompanied by a substantial decrease of the aromatic content of OME (up to 76%) which was adequate to enhance the subsequent aerobic degradation. Experiments with a more concentrated OME (COD ≈ 60 g dm<sup>-3</sup>) showed that ozonation for 8 h led to 6.2% COD and 94.3% total phenols reduction.<sup>67</sup> The nearly complete removal of phenols reduced the associated toxicity to methanogenic bacteria and facilitated the anaerobic digestion of OME. Ozone selectivity towards the phenolic content of OME has also been demonstrated by Andreozzi *et al*<sup>64</sup> who reported 65% total phenols reduction after 5 h of ozonation at pH 8; under these conditions, the initial COD value of about 122 g dm<sup>-3</sup> remained practically unchanged. However, unlike the results of Benitez *et al*<sup>67</sup> ozonation by-products were more toxic to methanogens than the original effluent.

The effect of operating conditions (hydrogen peroxide and iron concentration, reaction temperature) on OME treatment (COD = 95 g dm<sup>-3</sup>) by means of Fenton oxidation was studied by Beltrán-Heredia *et al*<sup>38</sup> who reported COD and total phenols reductions up to about 33% and 94% respectively after 8 h of treatment. In other studies, Rivas *et al*<sup>45</sup> found that Fenton treatment of dilute OME (COD ≈ 15 g dm<sup>-3</sup>) was capable of reducing the COD content and total phenols by as much as 85–90% and 100% respectively after 3–4 h at 50 °C. Moreover, the same effluent was subject to WAO<sup>87</sup> for 6 h at 180 °C and  $P_{\text{tot}} = 7$  MPa after which 30% COD and 80% total phenols reduction was achieved; the oxidized effluent was more biodegradable aerobically than the untreated OME. These studies show that a sequential chemical and biological treatment may be ideally suited to OME since mild chemical oxidation by various AOPs and WAO processes can easily convert biorecalcitrant fractions (eg polyphenols) to more readily biodegradable intermediates.

Although complete mineralization by means of chemical oxidation is plausible, this would require

harsh treatment conditions and consequently become prohibitively expensive. Rivas *et al*<sup>108</sup> reported that OME treatment by super-critical WAO at temperatures up to 500 °C and  $P_{\text{tot}} = 25$  MPa was capable of decontaminating completely (eg 99.9% COD removal) the effluent in 1–3 min. Israilides *et al*<sup>100</sup> who investigated the electrochemical treatment of OME (COD = 178 g dm<sup>-3</sup>) over a Ti/Pt anode using NaCl as the electrolyte reported that complete mineralization (eg 93% COD and 99.4% total phenols reduction) would require 12.3 kWh per kg of COD removed, thus making the process economically unattractive. However, using electrochemical oxidation as the pre-treatment step prior to biological post-treatment to achieve 76% COD and 93% total phenols reduction would require only 4.7 kWh per kg of COD removed. In further studies, Rivas *et al*<sup>45</sup> estimated that OME treatment by Fenton oxidation would cost USD 3.2 per m<sup>3</sup> of wastewater treated and g dm<sup>-3</sup> of COD removed which is far more expensive than the cost of biological treatment. Fiestas Ros de Ursinos and Borja-Padilla<sup>109</sup> who developed a sophisticated three-stage aerobic–anaerobic–aerobic process for OME treatment reported running costs in the order of USD 0.1 per m<sup>3</sup> of wastewater treated and g dm<sup>-3</sup> of COD removed.

#### 4.1.2 Effluents from table olive processing

Production of table olives is another common activity in Mediterranean countries that generates highly contaminated effluents during different manufacturing stages including debittering of fruits with NaOH, washing with water or dilute NaCl solutions (brines) and fermentation.<sup>24,86</sup> Depending on the stage these effluents come from, they are characterized by moderate to large COD and BOD contents and also contain considerable amounts of polyphenols and other aromatic compounds as well as inorganic salts; furthermore, they are strongly alkaline with pH values greater than 12. For instance, washing effluents<sup>39,51</sup> may have COD contents between about 2.5 and 6 g dm<sup>-3</sup>, while debittering effluents<sup>110</sup> may have COD values up to 25 g dm<sup>-3</sup>. In common practice, washing and debittering streams are merged and dumped untreated into evaporation ponds.<sup>24</sup>

In this respect, recent studies have dealt with the use of advanced oxidation as a suitable pre-treatment method for this type of waste. Given the high alkalinity of table olive processing effluents, ozonation appears to be an attractive treatment option since ozone can react rapidly with polyphenols through a combination of direct attack and hydroxyl radical-induced reactions. This has been demonstrated in several studies where ozone pre-treatment was capable of removing most of the phenolic compounds present in black olives mixed washing and debittering effluents,<sup>24</sup> black olives washing effluents,<sup>39,51</sup> black olives debittering effluents<sup>110</sup> and green olives mixed washing and debittering effluents;<sup>111</sup> in all cases, pre-treatment enhanced subsequent biodegradability.

Coupling ozonation with UV irradiation (with or without hydrogen peroxide) has also been studied<sup>24,110</sup> and found capable of improving the efficiency of single ozonation; this was attributed to increased occurrence of hydroxyl radical reactions. It should be mentioned that following chemical pre-oxidation the resulting effluent is nearly neutral (eg pH = 7.5–8.5) due to the formation of acidic by-products; this is important since little or no pH adjustment is needed prior to biological degradation.

Information regarding treatment of table olive processing effluents by WAO is scarce. Rivas *et al*<sup>86</sup> employed WAO (with and without Cu<sup>2+</sup> or hydrogen peroxide) to treat an effluent from green olives processing with an initial COD and total phenols content of about 12–15 g dm<sup>-3</sup> and 0.3–0.5 g dm<sup>-3</sup> respectively. A 30% COD and 90% total phenols reduction was recorded after 6 h of uncatalysed WAO at 180 °C and  $P_{\text{tot}} = 5$  MPa; these values increased to 37% and 94% respectively in the presence of about 0.4 g dm<sup>-3</sup> Cu<sup>2+</sup> (without H<sub>2</sub>O<sub>2</sub>) and to 35% and 92% respectively in the presence of 0.34 g dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> (without Cu<sup>2+</sup>). Effluents treated by uncatalysed or H<sub>2</sub>O<sub>2</sub>-promoted WAO were more readily biodegradable aerobically than the original effluent. Conversely, effluents treated by catalytic WAO were less biodegradable presumably due to the presence of toxic copper; this highlights the need to recover homogeneous catalysts from the treated effluent prior to discharge or subsequent biodegradation.

#### 4.1.3 Effluents from wine distilleries

Ethanol production from wines and pressed grapes generates acidic effluents (eg pH = 3.5–5) with COD values in the range 10–40 g dm<sup>-3</sup> and the organic matter mainly consisting of phenols, polyphenols, carbohydrates and acids.<sup>7,56</sup> Although such effluents (commonly referred to as vinasses) are partly biodegradable, increased treatment efficiencies can be achieved combining biological treatment with chemical pre-oxidation. This has been demonstrated by Benitez *et al*<sup>7</sup> and Beltrán *et al*<sup>49</sup> who found that an integrated ozonation–activated sludge process was more effective than each individual process alone.

## 4.2 Effluents from textile industries

Textile manufacturing involves several processes (eg sizing of fibres, scouring, de-sizing, bleaching, rinsing, mercerizing, dyeing and finishing) which generate large quantities of wastewaters. These effluents are highly variable in composition with relatively low BOD and high COD contents and are typically characterized by: (i) strong colour due to residual dyes, (ii) recalcitrance due to the presence of compounds such as dyes, surfactants and sizing agents, (iii) high salinity (up to 100 g dm<sup>-3</sup> NaCl) and (iv) high temperature and highly variable pH.<sup>32,98</sup> Increasing environmental concerns regarding the treatment and safe disposal of textile effluents have led to the

introduction of strict discharge limits all over the world. For instance, the discharge levels (averaged over 30 consecutive days) set by the US EPA for effluents from the yarn dyeing and finishing processes should not exceed 42.3 g COD per kg of product, while similar limitations apply for effluents from other textile activities.

Given the complex and bioresistant character of textile effluents, their effective treatment usually requires a combination of various physical, chemical and biological technologies. In view of this, several AOPs have been employed as a pre-treatment method aiming at reducing effluent colour and biorecalcitrance.

Ledakowicz *et al.*<sup>42</sup> and Ledakowicz and Gonera<sup>43</sup> compared various AOPs, namely ozonation, UV irradiation, H<sub>2</sub>O<sub>2</sub> oxidation as well as all possible combinations of the above to treat a synthetic dyehouse effluent with COD = 2.2 g dm<sup>-3</sup>. They reported that nearly complete colour removal could be achieved after 90 min of oxidation with ozone, while UV irradiation was less effective, resulting in 90% removal. All AOPs were capable of detoxifying the effluent which could then be treated by activated sludge. TiO<sub>2</sub> photocatalysis was employed to treat a dilute wool textile effluent with COD = 0.12 g dm<sup>-3</sup>.<sup>58</sup> Treatment for 30 min was sufficient to achieve complete colour removal, 45% COD removal and improve the aerobic biodegradability of the effluent (eg the BOD<sub>5</sub>/COD ratio increased from 0.26 to 0.39). Ahn *et al.*<sup>55</sup> proposed a three-stage process comprising Fenton pre-oxidation followed by activated sludge biofilm and Fenton post-oxidation for the complete treatment of a disperse dyestuff effluent with COD = 9.2 g dm<sup>-3</sup>. Fenton pre-treatment for 60 min was capable of achieving 60–80% COD reduction depending on the concentrations of H<sub>2</sub>O<sub>2</sub> and iron used. The residual COD was nearly completely removed by activated sludge treatment at residence times up to 23 h; the final effluent with a COD content of about 0.6 g dm<sup>-3</sup> could be polished by Fenton oxidation to bring COD down to 0.1 g dm<sup>-3</sup> (eg this corresponds to 99% overall COD reduction). In further studies, Germirli-Babuna *et al.*<sup>59</sup> employed Fenton oxidation to improve the biological properties of a yarn and fibre dyeing effluent with COD = 1.9 g dm<sup>-3</sup>. Depending on the dosage of H<sub>2</sub>O<sub>2</sub> used, the extent of COD reduction varied between 48% and 67% after 1 day of treatment. Rodriguez *et al.*<sup>32</sup> proposed a photo-Fenton process to treat a textile effluent with COD = 4 g dm<sup>-3</sup>. They studied the effect of operating conditions such as H<sub>2</sub>O<sub>2</sub> and iron concentration and reaction temperature on the extent of mineralization and determined optimal treatment regimes. Nonetheless, chemical pre-treatment did not manage to improve the poor biodegradability of the original effluent.

Lin and Peng<sup>76</sup> developed a continuous process comprising coagulation, electrochemical oxidation and activated sludge to treat dyeing and finishing effluents. Polyaluminium chloride (PAC) was used as the coagulant and the effluent, following sedimentation for

60 min, was subject to electrochemical oxidation. The partially treated effluent was then sent to a second sedimentation tank for 30 min and the supernatant was finally subject to activated sludge treatment. The effect of changing operating conditions such as PAC concentration, solution pH, current density, number of electrodes, residence times in electrochemical and biological reactors on treatment efficiency was thoroughly investigated and optimal conditions were established. Coagulation with 40 mg dm<sup>-3</sup> PAC decreased the COD content of the effluent from 0.7 g dm<sup>-3</sup> to 0.4 g dm<sup>-3</sup>, while electrochemical oxidation for 18 min at 30 A current resulted in an effluent with about 0.24 g dm<sup>-3</sup> COD. The effluent was finally subject to aerobic degradation for 60 min at the end of which the remaining COD was 0.1 g dm<sup>-3</sup>, well below the discharge limit of 0.2 g dm<sup>-3</sup> set by the Taiwan EPA. Moreover, the transparency of the effluent was about 30 cm, twice as much as the minimum acceptable value. The cost of the proposed treatment was estimated at USD 0.34 per ton of effluent, which was 24% cheaper than that of the conventional treatment.

In addition to the work with actual or synthetic textile effluents, several recent studies deal with the treatment of model solutions containing commercial dyes. Particular emphasis has been given to azo dyes since they are extensively used in dyeing processes. Azo dyes contain one to four azo groups usually attached to two radicals of which at least one, but usually both, are aromatic groups. These molecules are chemically stable and hardly biodegradable aerobically. Although they are easily reduced under anaerobic conditions, they produce potentially more hazardous aromatic amines. It is notable that the European Commission has banned the use of azo dyes which, by reductive cleavage, may release certain amines at concentrations greater than 30 mg dm<sup>-3</sup> (Council Directive 2002/61/EC).

In this respect, chemical oxidation appears to be a suitable treatment method for azo dyes. Special attention has been paid on the oxidative degradation of model aqueous solutions of Orange II (C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>NaO<sub>4</sub>S), a biorecalcitrant mono-azo dye typically found in dyehouse effluents. Several recent studies concerning the kinetics and mechanisms of Orange II degradation by means of TiO<sub>2</sub> photocatalysis,<sup>112,113</sup> ozonation,<sup>72,114</sup> photo-Fenton oxidation,<sup>115</sup> electrochemical oxidation,<sup>116,117</sup> sonolysis and  $\gamma$ -radiolysis<sup>118</sup> and uncatalysed and catalytic WAO<sup>94,95,119</sup> are available in the literature. Some of these studies also report improvements in the BOD<sub>5</sub>/COD ratio of Orange II solutions subject to ozonation and WAO.<sup>72,94,95</sup>

### 4.3 Effluents from pulp and paper mills

Pulp and paper bleaching effluents typically contain, amongst several others, refractory chlorinated organics that need to be destroyed prior to biological treatment. Photocatalysis over TiO<sub>2</sub> or ZnO was found capable of increasing the aerobic biodegradability



as well as decreasing the acute toxicity of a pulp bleaching effluent with initial COD  $\approx 1.6 \text{ g dm}^{-3}$  and BOD<sub>5</sub>/COD  $\approx 0.3$ .<sup>63</sup> Photocatalytic treatment for 1 min resulted in 44% and 51% COD reduction with ZnO and TiO<sub>2</sub> respectively; this was accompanied by an increase of the BOD<sub>5</sub>/COD ratio to values greater than 0.5 as well as a 50% reduction of acute toxicity for both catalysts. Coupling photocatalysis for 1 min with activated sludge treatment for 3 days resulted in 62% and 70% overall COD reduction with ZnO and TiO<sub>2</sub> respectively; the corresponding value for direct biological treatment was 58%. The use of high frequency (500 kHz) ultrasound to improve the biological properties of an acidic paper mill effluent with initial COD =  $2 \text{ g dm}^{-3}$  and BOD<sub>5</sub>/COD = 0.11 has been demonstrated in recent studies.<sup>14</sup> Sonication at  $42 \text{ GJ m}^{-3}$  of specific energy resulted in 41% COD reduction and 38% BOD<sub>5</sub> increase, thus showing a clear improvement of effluent's aerobic biodegradability. At a specific energy of  $142 \text{ GJ m}^{-3}$ , both COD and BOD<sub>5</sub> decreased by about 85% and 55% respectively resulting in a BOD<sub>5</sub>/COD ratio of 0.29. At the same time, effluent's inhibition to bioluminescence (*Vibrio fischeri*) decreased from 60% to about 20%. Nonetheless, ultrasound proved inadequate to treat a concentrated pulp effluent with COD =  $15 \text{ g dm}^{-3}$ ; sonication at  $40 \text{ GJ m}^{-3}$  led to neither COD nor toxicity reduction.

On the other hand, concentrated paper mill effluents with inlet COD up to about  $20 \text{ g dm}^{-3}$  and BOD/COD  $\approx 0.4$  were treated successfully by uncatalysed and catalytic WAO operating at temperatures between 130 and 200 °C and  $P_{\text{O}_2} = 1 \text{ MPa}$ .<sup>91</sup> Treatment for 2 h at 150 °C with and without Cu<sup>2+</sup> homogeneous catalyst led to about 60% and 40% COD reduction respectively. In both cases, the final BOD/COD ratio was 0.7. The authors also estimated operating costs for a WAO unit treating  $50 \text{ m}^3 \text{ h}^{-1}$  of pulp effluent with COD =  $20 \text{ g dm}^{-3}$  at 150 °C. To achieve 50% COD reduction would cost USD 0.44 per m<sup>3</sup> of effluent treated (or USD 0.04 per kg COD removed) using air at 5.5 MPa as the oxidant; the cost would increase to USD 1.1 per m<sup>3</sup> of effluent treated (or USD 0.11 per kg COD removed) if pure oxygen at 1.5 MPa were used. Interestingly, activated sludge treatment costs were estimated at about USD 0.11 per kg COD removed. In a recent study<sup>78</sup> WAO over TiO<sub>2</sub> and Ru/TiO<sub>2</sub> heterogeneous catalysts was employed to treat two pulp bleaching effluents with inlet COD of  $2.9 \text{ g dm}^{-3}$  and  $3.6 \text{ g dm}^{-3}$ . Ru/TiO<sub>2</sub> was substantially more active than TiO<sub>2</sub> leading to over 95% COD and TOC reduction for both streams at 190 °C and  $P_{\text{tot}} = 5.5 \text{ MPa}$ . Despite the deep mineralization, the treated effluents were more toxic to *Daphnia magna* than the original streams. Increased toxicity was attributed to the cumulative effects of acetic acid (a stable by-product of WAO) and inorganic salts originally present in the effluents.

#### 4.4 Effluents containing heavy metals and inorganic salts

Industrial effluents often contain toxic metals that need to be removed or recovered prior to biological treatment or discharge. The most commonly employed method for heavy metals removal is chemical precipitation. Although this approach is relatively simple and inexpensive, it has the disadvantage of generating large volumes of sludge for disposal. In addition to this, the treated effluent may contain residual coagulants whose removal requires further treatment. Alternative methods include solvent extraction, ion exchange, reverse osmosis, ultrafiltration and electrolysis. However, the use of an extra process for heavy metals removal increases inevitably treatment costs. In light of this, the application of AOPs for the simultaneous treatment of heavy metals and refractory organics has been investigated.

An innovative technology, namely electrochemical peroxidation, was developed to treat effluents containing heavy metals and organic contaminants.<sup>120</sup> The process utilizes steel electrodes and H<sub>2</sub>O<sub>2</sub> as follows: applying direct current, steel leaches in the aqueous phase as Fe<sup>2+</sup> which reacts with H<sub>2</sub>O<sub>2</sub> to form Fe<sup>3+</sup>; the latter readily precipitates as hydrous ferric oxide which acts as adsorbent for various metals. The process has been employed to remove completely metals such as arsenic, chromium and lead from water. In addition to this, it has been employed for the electro-Fenton oxidation of organic pollutants such as polychlorinated biphenyls, petroleum hydrocarbons, chlorinated solvents and MTBE. Chaudhary *et al*<sup>121</sup> proposed a combined electrochemical and photochemical process for the treatment of model aqueous solutions containing  $0.5 \text{ g dm}^{-3}$  Cu(II) and  $0.05 \text{ g dm}^{-3}$  EDTA. Electrochemical treatment alone was capable of achieving 80% copper recovery and 38.9% EDTA degradation after 8 h, while the respective values for photochemical treatment alone were zero and 87.7%. Coupling the two processes resulted in 90% copper recovery and 96.5% EDTA degradation with these values increasing to 94.3% and 99.2% respectively with the addition of  $5 \text{ cm}^3 \text{ dm}^{-3}$  H<sub>2</sub>O<sub>2</sub>.

Simultaneous treatment of a solution containing Cr(VI) and phenol at various concentrations by TiO<sub>2</sub> photocatalysis has been demonstrated by Lee *et al*.<sup>122</sup> Phenol undergoes oxidative degradation, while Cr(VI) is reduced to Cr(III); the latter is non-carcinogenic as well as considerably less toxic and mobile than Cr(VI) and can easily be removed from the aqueous phase by precipitation. Other than Cr(VI), metals such as Hg(II), Cu(II), Ag(I), Au(III) and Pt(IV) have also been treated by TiO<sub>2</sub> photocatalysis in the presence of organic compounds such as phenol, aniline and salicylic acid.<sup>123</sup>

Effluents such as those from textile industries and table olive processing typically contain considerable concentrations of inorganic salts and acids. Increased salinity may have several effects on treatment, the most common of which are:

- (i) several salts act as radical scavengers; consequently, the oxidant is consumed through wasteful reactions;
- (ii) in the case of electrochemical treatment, NaCl is likely to advance degradation through the generation of chlorine and other oxidants. However, this may be offset by the potential formation of hazardous chlorinated by-products;
- (iii) salts decrease the solubility of organics in the aqueous phase (salting-out effect), thus altering the kinetics and mechanisms of chemical oxidation;
- (iv) excessive salinity may impede biological treatment.

## 5 MEASURING THE CHEMICAL PRE-TREATMENT EFFECT

As has already been discussed, the primary role of chemical pre-treatment is the partial oxidation of bioreistant fractions to biodegradable intermediates. Total oxidation should be kept to a minimum during pre-treatment in order to avoid unnecessary waste of the chemical oxidant and energy, thus reducing treatment costs. The parameter used most commonly to describe the performance of pre-treatment is reduction of lumped concentrations such as TOC and COD. TOC is proportional to the concentration of organics in the liquid and is limited to describing total oxidation as it remains unchanged at mild treatment conditions where little or no total oxidation occurs. On the other hand, COD data on its own cannot differentiate between partial and total oxidation since both reactions contribute to a decrease of its value. Therefore, TOC and COD, if used in an isolated way, provide little useful insight with respect to partial oxidation.

Jochimsen and Jekel<sup>71</sup> proposed the use of a partial oxidation parameter ( $COD_{\text{partox}}$ ) which compares COD/TOC ratios at different treatment times to the initial ratio as follows:

$$COD_{\text{partox}} = (COD_{\text{initial}}/TOC_{\text{initial}}) - (COD/TOC)_{\text{TOC}} \quad (1)$$

where  $COD_{\text{partox}}$  refers to COD reduction via partial oxidation alone. The efficiency of COD removal via partial oxidation ( $\mu$ ) is then defined as follows:

$$\mu = (COD_{\text{partox}})/(COD_{\text{initial}} - COD) \quad (2)$$

$\mu$  reaches the value of 1 for the ideal case where no total oxidation occurs and 0 when only total oxidation occurs.

In further studies<sup>124</sup>  $COD_{\text{partox}}$  was used to evaluate the number average MW of a polyethylene glycol-containing effluent subject to mild WAO. A correlation between  $COD_{\text{partox}}$  and the number of bond scissions occurring during partial oxidative degradation of the polymer was proposed and provided a rapid and

relatively reliable assessment of the degree of polymer fragmentation.

Another way to combine TOC and COD data has been proposed by Scott and Ollis<sup>3</sup> as follows:

$$AOSC = 4(TOC-COD)/TOC \quad (3)$$

where AOSC is the average oxidation state of carbon in the aqueous phase and COD, TOC are expressed in molar concentrations. AOSC takes values between -4 (eg methane) and +4 (eg CO<sub>2</sub>) with high values indicating a high oxidation state of the organics in the liquid. The main drawback associated with the use of AOSC is that it cannot indicate how much partial and total oxidation has taken place since the start of the reaction. Clearly this parameter only reflects the oxidation state at one given time and it cannot be used for assessing the progress of partial oxidation reactions.

Regarding the biological step, the effect of chemical pre-treatment on the properties of the effluent is usually assessed by means of:

- (i) biodegradability tests,
- (ii) toxicity tests,
- (iii) integrated studies where the partially treated effluent is fed to biological post-treatment,
- (iv) a combination of the above.

The standard BOD test has been commonly employed as a measure of aerobic biodegradability. Changes in biodegradability are assessed by measuring the  $BOD_x/COD$  and/or  $BOD_x/TOC$  ratios and comparing the values of the treated samples with those of the original effluents. These ratios give a gross index of the proportion of the organic materials present which are aerobically degradable within a certain period of time (eg 5 days for BOD<sub>5</sub>). The drawbacks of using BOD for assessing the aerobic biodegradability of organics have been recognized since the early 1950s. The limitations of the BOD test arise mainly from the fact that the microorganisms may not be adapted to utilize the organics present, while the rate of biodegradation also appears to vary with concentration. Bearing these in mind, BOD results should be interpreted with caution and may not be directly comparable to data coming from other sources. Another point of concern is that quoting values of the  $BOD_x/COD$  (or  $BOD_x/TOC$ ) ratio alone may be misleading unless individual BOD<sub>x</sub> and COD (or TOC) values are also given. This is so since, in several cases, a substantial COD reduction occurring during chemical pre-treatment rather than an increase in BOD<sub>x</sub> is responsible for increased ratios of biodegradability. Other than the BOD test, aerobic biodegradability is also assessed by means of shake flask tests, respirometry and the Zahn-Wellens test. Anaerobic biodegradability tests are less popular and usually measure the rate of biogas production (eg biochemical methane potential test).

Acute toxicity to freshwater microorganisms such as *Daphnia magna* and *Selenastrum capricornutum* and marine microorganisms such as *Vibrio fischeri*, *Photobacterium phosphoreum* and *Artemia salina* has been measured in several studies and the results are usually quoted in the form of EC<sub>50</sub> values. Levels of toxicity during chemical pre-treatment appear to be a strong function of the treatment conditions. In several cases, toxicity of the original effluent was found to increase steeply and reach a maximum during the early stages of the pre-treatment presumably due to the formation of toxic intermediates.<sup>14,22,23,29,31,34,35,73</sup> At longer treatment times, toxicity decreases to acceptable levels as toxic intermediates are degraded further. It should be pointed out that an increase in the toxicity following oxidation is not necessarily accompanied by a decrease in biodegradability. Wang *et al*<sup>23</sup> who studied the ozonation of azo dye Remazol Black reported that samples subject to ozonation for up to 150 min were more biodegradable (in terms of increased BOD<sub>5</sub> and BOD<sub>28</sub> values) but also more toxic to *Vibrio fischeri* and rat hepatoma cells than the original effluent.

Although biodegradability and toxicity assays provide some useful information with respect to the effect of chemical pre-treatment, trials integrating chemical and biological degradation experiments are often needed to obtain an additional, more realistic assessment of the combined process. Several recent studies have comprehensively addressed this issue, employing various biological degradation schemes. In most cases, post-treatment comprises aerobic degradation in stirred tank or fixed bed reactors with sludge taken from domestic wastewater treatment plants. An interesting point associated with biodegradation experiments is whether acclimated or non-acclimated microorganisms should be used to maximize degradation efficiency. Contreras *et al*<sup>10</sup> reported that biodegradation of 2,4-dichlorophenol subject to ozonation with non-acclimated activated sludge was more efficient than that with sludge adapted to phenol (a primary ozonation intermediate). This implies that a non-acclimated culture may have a larger number of species which are more adaptable in degrading oxidation intermediates. Moreover, if acclimation is used, what should microorganisms be adapted to? For example, the original effluent, chemical oxidation intermediates or both? Rivas *et al*<sup>86</sup> found that biodegradation of a wet oxidized table olive-processing effluent with biomass adapted to oxidation intermediates was faster than that with biomass adapted to the original effluent. In most studies though, effective biodegradation with cultures adapted to the original effluent has been reported; however, comparison with non-acclimated cultures or cultures adapted to different substrates is not made and, therefore, safe conclusions cannot be drawn.

In contrast to the volume of work regarding aerobic degradation, few studies report the use of anaerobic degradation as the biological treatment stage.<sup>44,67</sup>

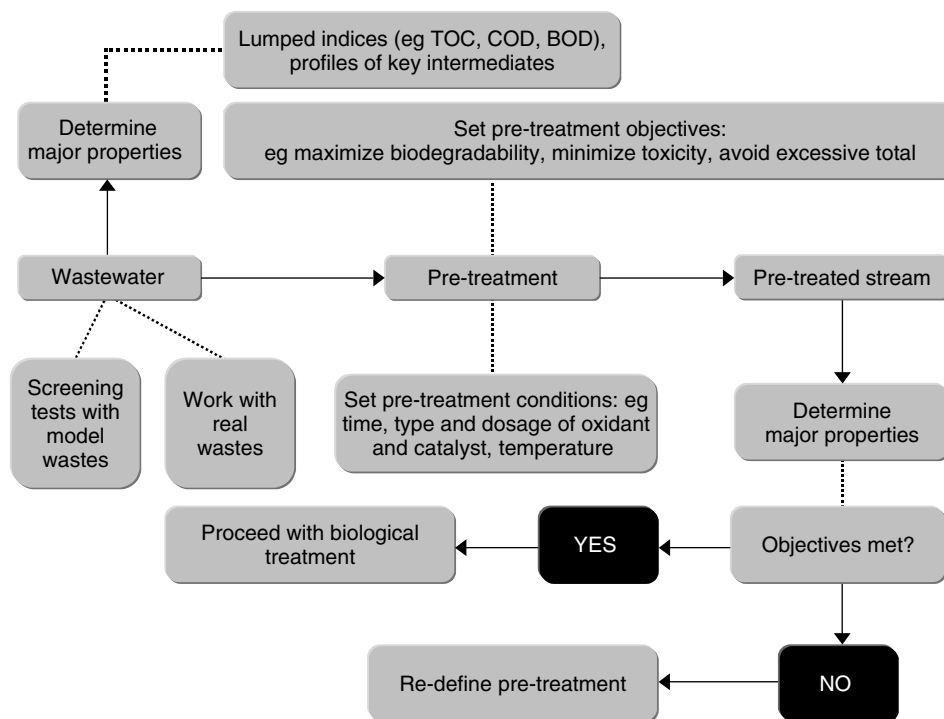
## 6 RESEARCH METHODOLOGY

About two-thirds of the studies reviewed show that chemical pre-treatment has a clear beneficial effect on subsequent biodegradability and/or toxicity. There are, however, cases where chemical pre-treatment, although conceptually advantageous, has an insignificant or even detrimental effect on the properties of the original effluent. This may be due to several reasons, the most common of which are:

- (i) Formation of stable intermediates that are less biodegradable than the starting molecules.
- (ii) Lack of selectivity during chemical pre-treatment to attack bioresistant rather than biodegradable fractions.
- (iii) Poor selection of treatment conditions. For instance, very mild pre-oxidation does not suffice to inflict serious changes on the properties of the effluent; on the other hand, excessive pre-oxidation may lead to effluents that possess little metabolic value for the microorganisms.
- (iv) No action is taken to remove the excess of oxidant and/or catalyst used in certain oxidation schemes. Compounds such as ozone and hydrogen peroxide (both of which are well-known disinfectants), metals, metal oxides and metal salts (catalysts in several processes) are usually toxic to microorganisms.

The aforementioned limitations highlight the need to establish a step-by-step research methodology which is schematically shown in Fig 4. To design an integrated treatment on a rational basis, the routes through which chemical oxidation enhances biodegradability should be thoroughly examined and understood. This is so since chemical pre-treatment will greatly affect the performance of the subsequent biological step and eventually determine overall efficiencies. Therefore, detailed studies with respect to the effect of operating conditions (eg contact time, type, dosage and toxicity of oxidant and/or catalysts, temperature) on the primary properties of the pre-treated stream are needed; such investigations necessitate the use of state-of-the-art analytical tools, elucidation of reaction mechanisms, pathways and kinetics, and an assessment of chemical pre-treatment on the biodegradability employing various degradability and toxicity tests.

The extent to which chemical pre-treatment is studied is usually determined (and restricted) by the type of effluent in question. Depending on its complexity as well as the availability of analytical resources, characterization could range between measuring gross parameters such as TOC and COD (eg in the case of actual wastes) and individual compounds concentration profiles (eg in the case of single-component synthetic solutions). It is evident that working with real-world wastes unavoidably compromises the quantity and quality of information that can be obtained; the exact composition of the original effluent is hardly known,



**Figure 4.** A step-by-step approach to evaluate chemical pre-treatment performance.

identification of reaction intermediates is practically unfeasible, kinetics have to be based on TOC or COD measurements. On the other hand, studies with model, representative effluents provide useful information regarding the crucial early stages of chemical pre-treatment. However, this information cannot be directly applied to actual wastes given the vast differences between model and real effluents. We believe that bridging the gap between the two extremes requires a string of experimental studies starting from model solutions prior to moving to more complex and eventually to real effluents. This step-by-step and often laborious approach has not been extensively used in previous studies.

## 7 MODELLING STUDIES

The literature suggests that, unlike the sizeable amount of experimental data available, there is little information on mathematical models to describe each individual step and, more importantly, the overall process. Few studies have attempted to model the kinetics of the main processes involved during treatment.<sup>38,50,56,57,77,83</sup> In these studies, chemical oxidation (eg WAO, ozonation or Fenton oxidation) is typically described by a first-order rate expression with respect to the organic substrate, which is expressed in terms of COD, BOD or other gross parameters such as the aromatic content of the effluent. Aerobic biodegradation is used as post-treatment and models based on Monod,<sup>77</sup> Contois<sup>38,50</sup> or Grau<sup>57</sup> kinetic expressions are assumed. In a recent study, Rivas *et al*<sup>125</sup> developed a comprehensive semi-empirical mechanistic and kinetic model to describe the treatment of table olive fermentation brines by means of sequential Fenton

oxidation and aerobic degradation. A set of 21 first-order differential equations was used to describe the kinetics of all plausible pathways occurring during the chemical oxidation step, while the Monod equation was used to model aerobic degradation. Their approach was validated experimentally and was found capable of predicting COD and H<sub>2</sub>O<sub>2</sub> concentration profiles during chemical oxidation as well as biomass growth during aerobic degradation. Moreover, the model adequately predicted the effect of changing dissolved oxygen concentration on COD removal but it failed to describe the respective effect of changing Fe<sup>3+</sup> concentration.

A common feature of the aforementioned studies is that they do not attempt to bring together the characteristic kinetic forms found in the individual processes; this would be necessary to develop overall, engineering models which are required for process design and economics and the determination of optimal operating conditions. Towards this direction is the work by Scott and Ollis<sup>126</sup> who developed a model capable of predicting the performance of a combined process comprising chemical oxidation in a continuous stirred tank reactor and aerobic biodegradation at different biological reactor configurations (eg chemostat, reactor with biomass recycle, plug flow reactor with immobilized cultures) and inhibitory biological kinetic regimes. Model simulations showed that a two-step process could achieve high treatment efficiencies at chemical reactor residence times substantially smaller (eg up to 14 times) than those required for a single-step chemical treatment, thus resulting in reduced treatment costs (eg up to five times in terms of chemical reactor capital cost). Moreover, optimal operating conditions were established with the total treatment

time (eg the sum of treatment times in chemical and biological reactors) set as a design constraint.

In further studies, Liakou *et al*<sup>72,127</sup> developed a kinetic model to describe the combined ozonation–aerobic degradation of azo dye Orange II. Concentration profiles of Orange II, ozone, three primary ozonation intermediates and COD during ozonation were successfully predicted by the model, while the Monod equation was used to model cell growth and substrate utilization during aerobic degradation. The overall model comprising 16 differential equations was coupled with several cost equations and used to estimate capital and operating costs for an integrated ozonation and activated sludge treatment plant treating 20 m<sup>3</sup> day<sup>-1</sup> of an effluent with an initial dye concentration of 0.5 g dm<sup>-3</sup>. To achieve 99.4% dye and 85% COD reduction would cost about USD 316 000 for a 30-year period of operation with 95% of the total cost accounting for the ozonation stage (eg capital cost of ozone generator and reactor and ozonation operating cost).

## 8 CONCLUDING REMARKS

The environmental, health and safety implications of biologically resistant, toxic or inhibitory organic contaminants in industrial wastewater discharges are causes for serious concern. A sequence of unit processes to treat such wastes may be advantageous or even necessary for efficient treatment. Chemical oxidation offers a promising treatment option for ‘difficult’ wastes. Processes such as photocatalysis, ozonation, Fenton oxidation and wet air oxidation have been widely employed for the complete or partial treatment of various classes of industrial effluents; in the latter case, chemical oxidation usually leads to the formation of more biodegradable intermediates, which can be post-treated biologically to yield efficient overall contaminant destruction. This process synergy has gained considerable attention over the past few years as indicated by the increasing number of peer-reviewed publications. These studies, mainly experimental in nature, comprehensively cover a wide spectrum of issues related to the treatment, eg evaluation of the impact of chemical oxidant and operating conditions in question on effluent properties, selectivity towards partial oxidation, determination of reaction kinetics and pathways, various configurations of biological post-treatment.

Photocatalytic oxidation and ozonation appear to be the most popular pre-treatment technologies compared with other AOPs as shown by the large amount of information available in the literature. The prevailing (but not exclusive) mechanism through which most AOPs function is the generation of highly reactive free radicals. Consequently, combination of two or more AOPs expectedly enhances free radical generation which eventually leads to higher oxidation rates. This synergy has been demonstrated in several studies reporting the use of Fenton’s reagent with UV

light (eg photo-Fenton process) or ozone with UV light and/or H<sub>2</sub>O<sub>2</sub>.

Wet air oxidation constitutes a relatively recent development in the field of chemical oxidation pre-treatment. The process can cope easily with highly concentrated effluents and usually operates under harsh treatment conditions to achieve nearly complete mineralization. Nonetheless, over the past decade WAO has also been employed under mild conditions where partial oxidation reactions of the organic substrate to potentially more biodegradable fractions dominate over total oxidation to carbon dioxide and water.

Beside the experimental work, it is also important to develop realistic and generalized kinetic and yet mechanistic models for predicting degradation rates and pathways for each individual step as well as for the integrated process; research in this area lags behind experimental work. More importantly, what the academic and industrial communities are really lacking is hard evidence that integrated chemical and biological treatment can be economically competitive in relation to other treatments. Few studies have, indeed, attempted basic cost estimates showing that chemical oxidation is, as expected, more expensive than conventional biological treatment. However, provided that direct biological treatment cannot be used for refractory effluents, it is necessary to compare integrated multi-stage schemes comprising different chemical pre-oxidation technologies with the respective single-stage chemical oxidation on the basis of total treatment costs.

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