Review

Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry: Review of Emerging Technologies

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Abstract: New ecolabels for textile products and tighter restrictions on wastewater discharges are forcing textile wet processors to reuse process water and chemicals. This challenge has prompted intensive research in new advanced treatment technologies, some of which currently making their way to full-scale installations. These comprise polishing treatments such as filtration, chemical oxidation and specialized flocculation techniques and pre-treatment steps including anaerobic digestion, fixed-film bioreactors, Fenton's reagent oxidation, electrolysis, or foam flotation. Though several of these new technologies are promising in terms of cost and performance, they all suffer limitations which require further research and/or need broader validation. A segment of the research deals with the separate handling of specific sub-streams such as dyebath effluents to which membrane filtration is sometimes applied. The main limitation of this approach is the treatment of the concentrate stream. The spectrum of available technologies may, in the future, be further broadened to include fungi/H2O2-driven oxidation, specialized bio-sorptive processes, solvent extraction, or photocatalysis. © 1998 SCI


Key words: textile; wastewater; dyes; azo; full-scale; activated sludge; filtration; coagulation; ozonation

NOTATION

AOX Adsorbable organic halogens
BOD Biological oxygen demand
Bv Volumetric loading rate
COD Chemical oxygen demand
HRT Hydraulic retention time
ICx Concentration causing x% inhibition
LCx Concentration causing x% lethality
MLVSS Mixed liquor volatile SS
NF Nanofiltration
NPE Nonyl phenol ethoxylate
RO Reverse osmosis
SRT Sludge retention time
SS Suspended solids
TS Total solids
TSS Total suspended solids
UASB Upflow anaerobic sludge blanket
UF Ultrafiltration
WWTP Wastewater treatment plant

1 INTRODUCTION

Considering both volume discharged and effluent composition, the wastewater generated by the textile industry is rated as the most polluting among all industrial sectors.1 In Flanders in 1994, four textile wet processors were among the six factories ranked with the
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largest annual BOD discharges. During the last few years, new and/or tighter regulations coupled with increased enforcement concerning wastewater discharges have been established in many countries. This new legislation, in conjunction with international trade pressures such as increasing competition and the introduction of ecolabels for textile products on the European and US markets, is threatening the very survival of the textile industry in many industrialized countries. The textile industry swiftly responded to these new constraints with a broad range of drastic changes and innovations in the generation, treatment, and reuse of textile wastewaters (Fig. 1). This review article is an attempt to summarize and compare the diverse innovative treatment technologies which have been used to treat and reuse textile effluents. The focus is placed on full-scale plants in order to be able to assess the new technologies in real situations.

2 THE NATURE OF TEXTILE EFFLUENTS

The main sources of wastewater generated by the textile wet-processing industry originate from the washing (or scouring) and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes, process aids and finishing products in use, these processes generate wastewaters of great chemical complexity and diversity which are not adequately treated in conventional WWTP. The chemical composition of textile mill effluents is also changing rapidly as a result of shifting consumers’ preferences. Most significant is the current popularity of cotton fabrics and bright colors leading to greater usage of reactive and azo dyes, respectively. An even more important cause of shifting wastewater composition are the new and tighter restrictions on discharged effluents and consumer goods as, for example, the 1996 German ban on consumer goods containing those azo dyes which cleave to yield any one of 20 specified carcinogenic aromatic amines. Another example is the emergence of US and European ecolabels which might include considerations of emissions to the environment and chemicals used during the manufacture of textile products. In response to these new restrictions, dye manufacturers are developing new lines of dyeing auxiliaries in order to comply with these ‘ecologically-advanced’ labels, e.g. emulsifiers not derived from alkyl phenols, pigments not containing halogeno substituents or heavy metals, chlorine-free bleaching agents, and synthetic thickening agents which reduce the amount of dye wasted.

The nature of textile wastewaters has already been reviewed in terms of process chemicals used and in terms of the classical parameters (BOD, COD, TSS, TS) and contents of N, P, and heavy metals. This section will therefore focus on those pollutants which often pose problems in conventional WWTP (as illus-

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**Fig. 1.** Compilation of possible process technologies, both commercial and experimental, for the treatment and reuse of final effluents of textile mills. 1: Alto Lura WWTP managed by CIDA Srl in the Como area (Italy) and treating 22 000 m$^3$ day$^{-1}$ of a mixture consisting of 17% domestic wastewater, 32% rain water and 51% equalized effluents from textile finishing factories (cellulose, wool, silk, and synthetic fiber). 2: Levi’s Strauss WWTP, Wervik (Belgium).
trated in the following section), i.e. dyes, recalcitrant organics, toxicants, AOX, and surfactants.

2.1 Color

Dye molecules consist of a chromagen, i.e. an aromatic structure absorbing visible light and which anchors the dye into or within the fibers. There are about 12 classes of chromogenic groups, the most common being the azo type which makes up to 60–70% of all textile dyestuffs produced, followed by the anthraquinone type. A second classification of dyes is based on their mode of application to textiles and distinguishes acid, reactive, metal-complex, disperse, vat, mordant, direct, basic and sulfur dyes. Research on textile effluent decolorization has often focused on reactive dyes for three reasons. First, reactive dyes represent an increasing market share, currently about 20–30% of the total market for dyes, because they are used to dye cotton which makes up about half of the world’s fiber consumption. Second, a large fraction, typically around 30%, of the applied reactive dyes is wasted because of dye hydrolysis in the alkaline dyebath. As a result, dyehouse effluents typically contain 0.6–0.8 g dye dm$^{-3}$. Third, conventional wastewater treatment plants, which rely on sorption and aerobic biodegradation, have a low removal efficiency for reactive and other anionic soluble dyes, which leads to colored waterways, and public complaints. As a result, new restrictions have been established for the discharge of colored effluents, e.g. in Germany and in the UK, often forcing dyehouses to decolorize their effluents on-site.

Since dyes are intentionally designed to resist degradation, it is no surprise that little dye degradation occurs in activated sludge systems. Among more than 100 azo dyes tested, only a very few were degraded this way. The degree of stability of azo dyes under aerobic conditions is proportional to the structural complexity of the molecule. While C.I. Acid Orange 7 (Fig. 2) is aerobically biodegradable, the 2-methyl derivative (C.I. Acid Orange 8) is less biodegradable, a related disulfonate dye (Acid Orange 10) is non-biodegradable. Under anoxic conditions, however, azo dyes are readily cleaved to aromatic amines since the azo bond can serve as electron acceptor in the electron transport chain provided a carbon source is available and nitrates absent. The by-products of the azo bond cleavage, aromatic amines, are not further metabolized under anaerobic conditions but are readily biodegraded in an aerobic environment. It is important to note that most types of dyes are partially degraded under anaerobic conditions, though less readily than azo dyes. The rate of degradation may be lowered by the dye’s structural complexity, as cell uptake was shown to be inversely proportional to the number of sulfonate groups, and moreover is subjected to inhibition in the presence of 15–100 mg dm$^{-3}$ of certain acid azo dyes.

2.2 Persistent organics

Due to a shift in process chemicals used, the biodegradability of textile wastewaters has been increasing steadily during recent years. In Flanders, for example, the BOD$_5$/COD ratio for the total wastewater discharged from textile wet processors increased from 0.18 in 1991 to 0.29 in 1994. The latter value, which is representative for the sector in other countries, points toward a moderately biodegradable organic load. The persistent molecules present in textile effluents belong to very diverse chemical classes, each used in relatively small amounts. Aside from dye molecules (see above), these include dyeing auxiliaries such as polyacrylates, phosphonates, sequestering agents (e.g. EDTA), defloculation agents (lignin or naphthalenesulfonates), antistatic agents for synthetic fibers, carriers in disperse dyeing of polyester, fixating agents in direct dyeing of cotton, preservatives (substituted phenol), and a large number of finishing auxiliaries used for fire-, moth-, and waterproofing. EDTA may amount to 1 g dm$^{-3}$ in reactive dyebath effluent. A particular case of persistence is the wash (scour) effluent of raw wool, consisting of a stable emulsion of detergents (0.8 g dm$^{-3}$ nonyl phenol ethoxylate), animal grease (15 g dm$^{-3}$ lanolin) and suint salts (animal secretions) together with the...
lipsoluble pesticides sprayed on the sheep for parasite control. Scouring of cotton also releases a great variety of persistent pesticides used in the growing of cotton. Finally, carpet factory effluents may contain latex which appears moderately biodegradable.

2.3 Toxicants

Textile effluents tend to inhibit only slightly, or not at all, the heterotrophic activity within activated sludges. This was illustrated by on-line toxicity measurements of the equalized effluent of a carpet factory in Flanders using the Rodtox sensor.\textsuperscript{34} During the 2-month-long data acquisition period, as part of the project financing this paper, the highest level of the heterotrophic respiration within sludge samples reached 10–20%. A 10–20% decrease of the COD removal capacity was also detected upon addition of various acid azo dyes to laboratory-scale activated sludge reactors\textsuperscript{35} or biofilm reactors.\textsuperscript{22} Less biofilm accumulation was also observed in the presence of the dyes.

Unlike heterotrophs, chemotrophic nitrifying bacteria are often substantially inhibited in activated sludges fed with textile effluents. Böhm\textsuperscript{36} measured oxygen uptake rate by nitrifiers in a fixed-bed reactor upon feeding with wastewater from two textile plants. The IC\textsubscript{25} values were 11 and 27% (v/v). Vandevivere and Verstraete (unpublished), using a short-term nitrification inhibition test, determined IC\textsubscript{50} values in the range of 10–40% (v/v) for the equalized effluents from two Flemish carpet factories. The inhibition was attributed mainly to copper chelators because addition of copper to the wastewater eliminated the inhibition. Grüttnner et al.\textsuperscript{37} singled out a textile dyeing factory as the most important source of nitrification inhibitors in an industrial catchment area in Denmark.

Numerous large-scale studies have been conducted to assess the toxicity of textile effluents toward aquatic life. Typical LC\textsubscript{50} (96 h) values amount to 5–6% (v/v) with bleaching, dyeing, or mixed textile effluents, using a freshwater fish as test organism.\textsuperscript{38} Costan et al.\textsuperscript{39} found that a textile effluent ranked second in toxicity, among eight industrial sectors represented, by using a series of bioassays assessing the acute, sublethal and chronic toxicity at various trophic levels. Using the Microtox assay, Undén\textsuperscript{40} ranked textile industries as heavy polluters among 49 Swedish industries tested. The actual process chemicals causing such harm remain unidentified. Unlawful discharge of organic solvents used in printing processes has at times been linked to effluent toxicity toward activated sludge (Bianchi, unpublished) or aquatic life.\textsuperscript{3} Extensive work has been dedicated to the potential toxicity of commercial dyes toward aquatic life. Since the exposure level in rivers is always much lower than the LC\textsubscript{50} values of the vast majority of dyes, these are not thought to cause acute toxicity to aquatic life.\textsuperscript{41,42} Data at chronic-level exposure are lacking for most of the commercial dyes and their derivatives\textsuperscript{17,43} and the potential toxicity of degradation intermediates remains therefore undocumented. Numerous dyes, together with the aromatic amines formed by reductive cleavage of azo bonds, are mutagenic.\textsuperscript{44}

2.4 Surfactants

Most textile wet processes, such as sizing, spinning, weaving, desizing, dyeing, scouring and washing consume large amounts of surfactants. Wool scour effluents may contain up to 800 mg dm\textsuperscript{-3} NPE.\textsuperscript{45} Combined municipal and textile effluents in the Como area contain peak concentrations of 11 and 67 mg dm\textsuperscript{-3} anionic and non-ionic surfactants respectively (Bianchi, unpublished) and the effluent of a silk and Lycra dyeing factory contained typically 30–40 mg dm\textsuperscript{-3} anionic surfactants. A large fraction of the non-ionic surfactants used in textile processes are alkyl phenol ethoxylates as the textile industry is the largest consumer of these surfactants.\textsuperscript{47} The issue is rather controversial in view of the fact that the discharge of alkyl phenol surfactants to sewers is often restricted, e.g. 0.5 mg dm\textsuperscript{-3} of phenol equivalents in Portugal, or even banned, e.g. in Germany.\textsuperscript{9} These restrictions were established because alkyl phenol polyethoxylate surfactants are biodegraded to alkyl phenols which tend to sorb onto and accumulate in sewage sludge wherein average concentrations up to 1000 ppm have been recorded.\textsuperscript{48,49} Alkyl phenols are, however, much more toxic than the ethoxylated forms, with maximum accepted concentration in the low ppb range.\textsuperscript{47} The discharge limit for other surfactants (in natural waters) is typically set at 2 mg dm\textsuperscript{-3} (Italy, Portugal).

2.5 AOX and heavy metals

Traditionally, sodium hypochlorite was usually preferred to H\textsubscript{2}O\textsubscript{2} for the bleaching of cotton and linen because of superior whiteness, lower cost and possible fiber damage by radicals arising from H\textsubscript{2}O\textsubscript{2} decomposition.\textsuperscript{50} Hypochlorite bleaching effluents contain up to 100 mg dm\textsuperscript{-3} AOX including considerable amounts of carcinogenic chloroform. Hypochlorite is being superseded by alkaline peroxide bleaching. Spent liquors from shrinkproofing with chlorine and mothproofing of wool may also contain AOX, up to 39 and 12 mg dm\textsuperscript{-3}, respectively.\textsuperscript{50} Finally, certain reactive dyes are AOX. Given their carcinogenic nature, the discharge of AOX is restricted in a number of countries including Belgium, Sweden, and Germany, with a discharge limit of 0.5 mg dm\textsuperscript{-3} in the latter country.\textsuperscript{9,50} Grüttnner et al.\textsuperscript{37} measured an average of 0.75 mg dm\textsuperscript{-3} AOX in the effluent of a textile dyeing factory.
Heavy metals concentrations in dyebath effluents, typically in the 1–10 mg dm$^{-3}$ range, were reviewed by Correia et al.$^{11}$ The use and discharge of heavy metals in the textile wet processing industry has decreased by an average of 50% in Flanders during the period 1991–1994.$^{30}$ In 1994, textile wastewaters in Flanders still typically contained about 0.15 mg dm$^{-3}$ of Cr and Cu (used as metal-complex dyes) and 0.8 mg Zn dm$^{-3}$.$^{30}$ Carpet factory effluents have higher concentrations of Cr and Ni (0.6–0.9 mg dm$^{-3}$) and Zn (1.9 mg dm$^{-3}$).

3 PERFORMANCE OF FULL-SCALE TREATMENT PLANTS

3.1 Full-scale plants relying solely on conventional activated sludge systems

The performance of activated sludge treatment is summarized in Table 1, together with other treatment technologies. In 1994, 27% of the wastewater generated by the textile mills located in Flanders was treated on-site and most of it subsequently discharged to surface waters.$^{30}$ Average effluent COD and BOD were 163 and 19 mg dm$^{-3}$, respectively, while total N and P amounted to 22 and 1 mg dm$^{-3}$, respectively. Such values exceed the tighter discharge norms established recently in many countries, with maximum permitted levels of COD and total N typically around 80 and 10 mg dm$^{-3}$, respectively. Because the above performance data apply to both conventional and advanced treatment, they probably overestimate the performance of conventional activated sludge systems. Other reports mention a 60–80% COD reduction in activated sludge plants$^{31,51}$ or laboratory-scale reactors.$^{52}$ Considering a typical COD content of 700 mg dm$^{-3}$ for textile effluents, these values correspond to c. 200 mg COD dm$^{-3}$ effluent. The performance of an activated sludge plant treating the effluent of a carpet factory in Flanders was followed for 4 months. Average effluent COD usually fell in the range 150–220 mg dm$^{-3}$ but peak values above 250 mg dm$^{-3}$ were frequently observed (Fig. 3; P. Van Meenen and B. Vanderhaegen, private communication).

Conventional activated sludge systems are clearly ineffective in decolorizing textile effluents even in cases where these are mixed and treated together with sewage. At the Pixton works (UK), the discharged effluent has an absorbance three times higher than the new discharge consent (though it should be noted that some of the new discharge consents in the UK specify extremely small absorbance values).$^{53}$ This leads to colored watercourses at the points of discharge and public complaints.$^3,5,54$ Primary settling removes relatively high

<table>
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<th>Process</th>
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<th>Status</th>
<th>Performance</th>
<th>Limitations</th>
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<tr>
<td>Fenton oxidation</td>
<td>Pre-treatment</td>
<td>Several full-scale plants in S. Africa</td>
<td>Full decolorization; low capital and running costs</td>
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<td>Electrolysis</td>
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<tr>
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<tr>
<td>Biodegradation Activated sludge</td>
<td>Main treatment</td>
<td>Widely used</td>
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<tr>
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<td>Main treatment</td>
<td>Very few reports</td>
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<tr>
<td>Fixed-bed</td>
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<td>Fungi/H$_2$O$_2$</td>
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<td>O$_3$</td>
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<td>Photocatalysis</td>
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proportions of insoluble disperse and vat dyes, while activated sludge removes medium to high proportions of soluble basic and direct dyes, principally by adsorption. On the other hand, the widely-used reactive and acid dyes are poorly removed.

Aside from COD and color removal, nitrification is occasionally impaired in sewage works receiving untreated textile effluents. At the Alto Lura WWTP (Italy), which treats a mixture of domestic and textile mills wastewaters, the NH$_4^+$-N content in the final effluent exceeded the discharge limit (11.8 mg dm$^{-3}$) on 47 days out of the 217 days monitored (Bianchi, unpublished). Similar problems were noted in a WWTP treating carpet effluents in Flanders, with NH$_4^+$-N level amounting to 9.2 ± 9.7 mg dm$^{-3}$ in the treated effluent (Fig. 3). Bortone et al. found that long SRT (up to 30–40 days) were necessary to overcome the nitrification inhibitory effect in bench-scale reactors treating a mixture of municipal and textile effluents. With respect to heavy metals, conventional WWTP designs do not achieve the discharge limits for surface waters, as Cr and Ni still amount to about 0.1 mg dm$^{-3}$ and Zn to 0.7 mg dm$^{-3}$ in the final effluent of the industrial treatment plants in Flanders.

Another problem with a seemingly high incidence in WWTP treating textile wastes are Nocardia foaming and filamentous bulking. While these are complex and poorly-understood phenomena, their frequent occurrence in WWTP receiving textile effluents may possibly be linked to high levels of starch and surfactants. NPE, a class of surfactants extensively used in the textile industry, together with their degradation intermediate nonyl phenol, are readily removed in activated sludge systems, with a removal efficiency lying between 92-5 and 99-8%. In a survey encompassing a large number of sewage works, treated effluents contained up to 261 ppb NPE and up to 94 ppb nonyl phenol. These low values do not necessarily reflect near-complete degradation since it was estimated that 60–65% of all NPE entering sewage works are in fact removed with the excess sludge.

### 3.2 Full-scale plants using sequential anaerobic/aerobic reactors or fixed film reactors

Several laboratory-scale investigations have illustrated the potential of sequential anaerobic/aerobic bio-treatment steps for textile wastewaters. Anaerobic pre-treatment offers several potential advantages such as better removal of color, AOX, and heavy metals. Improved heavy metal removal may follow sulfide production, while the improvement of the color and AOX removal stems from the rapid reduction and cleavage under anaerobic conditions of the azo groups in arylazo pollutants and of electron-withdrawing chloro or nitro substituents. Jianrong et al. achieved 90% COD reduction and 96% color reduction in a laboratory-scale UASB reactor (HRT = 8 h) followed by an activated sludge reactor (HRT = 6 h) fed with a deeply-colored high-strength effluent of a dye manufacturing plant. The greatest fraction of the color and COD reduction occurred in the UASB reactor. Other studies have shown, however, that methanogenesis, and hence COD removal, is easily inhibited by textile effluents. The inhibition of methanogenesis can be avoided by inserting granular activated carbon in UASB reactors treating textile effluents. This was demonstrated with a bench-scale set-up that achieved full decolorization and effluent COD level below 100 mg dm$^{-3}$ when fed with deeply-colored carpet factory effluents (Verstraete, not published). In cases where the inhibition of methanogenesis cannot be circumvented, anaerobic pre-treatment may remain useful as, for example, a decolorizing step, which seems to proceed optimally around a redox potential of −250 mV, or as a bioflocculation step. The latter may achieve high removal rates of poorly degradable organics such as the grease and detergents present in the very high-strength wool scouring effluents.

The effluent from a silk and Lycra printing factory in Como (250 m$^3$ day$^{-1}$) is being treated in a full-scale denitrification/nitrification single-sludge system. Operating conditions included the dosing of 22 mg dm$^{-3}$ sodium sulfide to remove Zn, the addition of 330 mg dm$^{-3}$ pharmaceutical waste in the denitrification reactor as a source of reducing equivalents, and the addition of 1 mg dm$^{-3}$ lyophilized bacteria to the nitrification plant. A tertiary treatment, consisting of quartz bed filtration and UV sterilization, has allowed 30–40% water reuse without deleterious effects on garment quality during 10 months of full-scale operation. Effluent COD (less than 120 mg dm$^{-3}$), color, and NH$_4^+$-N (less than 10 mg dm$^{-3}$) all met Italian discharge standards. The nitrification rate (0.03–0.05 g N
g\textsuperscript{-1} MLVSS, day\textsuperscript{-1}) was much lower than that which can be obtained with the municipal sewage. This low rate was attributed to inhibition caused by the presence of 30–40 mg dm\textsuperscript{-3} anionic surfactants in the wastewater. Both the Seveso and Alto Lura WWTP, located in Como (Italy), treat sewage containing 80% textile effluent. The Seveso plant, in which two-thirds of the influent passes through an ‘anaerobic selector’ (2 g COD g\textsuperscript{-1} MLVSS day\textsuperscript{-1} with an HRT of 45 min) performs better than the Alto Lura plant, which does not include such a selector.\textsuperscript{57} Increased performance was reflected in the elimination of the foaming and bulking problems, better P removal, and low effluent TSS (average of 20 mg dm\textsuperscript{-3} instead of more than 100 in Alto Lura).

Despite the numerous laboratory-scale trials showing the potential of anaerobic treatment for color removal, large-scale installations equipped with an anaerobic pre-treatment do not generally achieve full decolorization. Zaoyan \textit{et al.}\textsuperscript{64} operated a large pilot plant (24 m\textsuperscript{3} day\textsuperscript{-1}) for 9 months at a textile dyeing mill which used reactive and other dye classes on polyester/cotton fabric. The plant consisted of two multi-stage rotating biological contactors, a first anaerobic one (HRT = 7 h; \(B_1 = 2 \text{ g COD day}^{-1} \text{dm}^{-3}\)) followed by a second aerobic one (HRT = 5 h; \(B_2 = 2–3 \text{ g COD day}^{-1} \text{dm}^{-3}\)). The sequential anaerobic/aerobic system achieved a higher color removal (72%) than the aerobic system alone (<60%) but the final effluent was still deeply colored. Both systems achieved 78% COD removal (155 mg dm\textsuperscript{-3}), 95% BOD\textsubscript{5} removal (13 mg dm\textsuperscript{-3}) and 70% anionic surfactants removal (0.7 mg dm\textsuperscript{-3}). Another pilot two-stage anaerobic/aerobic plant achieved >70% color removal from dyeing wastewater.\textsuperscript{65} The Hammarsdale (South Africa) sewage works consists of a conventional five-stage bardenpho nutrient removal process treating deeply-colored textile effluents.\textsuperscript{62} Though the overall system achieves 95% decolorization, of which 60% takes place in the first anaerobic state (HRT of 1 h and redox potential of \(-135 \text{ mV}\)), the final effluent is still excessively colored. Since decolorization is fastest at \(-250 \text{ mV} \) (2–4 h), the color removal at the Hammarsdale works may be improved by increasing the HRT in the anaerobic stage.\textsuperscript{62}

Several experiments have been carried out in South Africa to investigate the possibility of feeding dyeebath effluents directly to the anaerobic digesters treating primary sludge from sewage works. Carliell \textit{et al.}\textsuperscript{33} mixed spent reactive dyeebath effluent with the primary sludge (6% v/v) entering the digester at Umbilo sewage works. Color was completely eliminated as shown by comparison with a control digester. Laboratory-scale side trials indicated, however, that methanogens may become inhibited after a few days operation at a higher loading (18%) due to the build up of sulfide originating from the 42 g dm\textsuperscript{-3} sulfate in the dyeebath effluent. Proposed measures to overcome the inhibition were the substitution of NaCl for sodium sulfate, the addition of heavy metals (e.g. from electroplating effluents) to precipitate the sulfides, or molybdate to block sulfureduction. Similar full-scale trials were carried out by Gravelet-Blondin \textit{et al.}\textsuperscript{3} for a period of 5 months. No color was present in the overflow of the digester but transport costs were considered prohibitive.

The combined activity of anaerobic/aerobic bacteria can also be obtained in a single step if the bacteria are immobilized in biofilms since O\textsubscript{2} penetration seldom exceeds several hundred micrometers.\textsuperscript{21} In addition to providing anaerobic/aerobic zones, fixed film reactors offer the advantages of higher SRT necessary to prevent washout of adapted microorganisms, protection against toxicants such as azo dye Acid Orange 7 (Fig. 2), and low sludge production.\textsuperscript{35} Laboratory-scale studies have demonstrated that acid azo dyes which are not degraded in activated sludge were removed up to 60% in fixed film reactors provided the dissolved O\textsubscript{2} concentration is kept below 1 mg dm\textsuperscript{-3} and the loading rate is high.\textsuperscript{32,35} Jian \textit{et al.}\textsuperscript{66} could treat the effluent from a dye manufacturing plant very effectively using multistage percolation columns with immobilized decolorizing bacteria. The pilot scale installation, which treated 20 m\textsuperscript{3} day\textsuperscript{-1}, removed consistently 97% of both color and COD during a 7-month trial.

### 3.3 Full-scale plants using a combination of activated sludge and coagulation/flocculation

Chemical coagulation is applied as either a pre-, post- or main process for the treatment of dyeing mill effluents (Fig. 1) and is, according to Gähr \textit{et al.},\textsuperscript{8} the treatment most widely used in Germany for these effluents. This author reports, however, the drawback associated with the large amounts of toxic sludge requiring combustion. Many French textile manufacturers likewise rely on a physico-chemical post-treatment, following activated sludge, to treat their colored effluents.\textsuperscript{31} Margagne and Coste\textsuperscript{31} contend that the final effluent usually contains from 150 to 300 mg dm\textsuperscript{-3} COD (85% removal) and color levels above the maximum discharge standard of 100 mg Pt-Co dm\textsuperscript{-3} which is expected to be enforced in France in the near future. Insufficient color removal is a result of the poor flocculation of certain types of dyes, e.g. reactive or certain acid dyes.\textsuperscript{31} For example, a mere 20% color removal was achieved in pilot experiments in which polyaluminum chloride (10 mg Al dm\textsuperscript{-3}) was dosed in the effluent of an activated sludge treating a mixture of municipal and textile wastewaters.\textsuperscript{67}

New flocculants have, however, been developed with a high affinity for reactive dyes.\textsuperscript{68,69} Several reports detail, for example, the successful use of cationic polymers allowing a few major UK textile processors to
meet their color consent for direct discharge to rivers.\textsuperscript{17,54} Dissolved air flotation can effectively separate the flocculated dyes with little sludge produced. At Livescia WWTP (Como, Italy) treating a mixture of municipal and textile wastewaters, a 35% color removal was obtained by dosing 20 mg dm\(^{-3}\) of cationic polymers in the effluent of the biological oxidation treatment (Bianchi, unpublished). Adequate color removal may be achieved by dosing cationic polymers directly to the activated sludge. The Wanlip sewage works (UK), receiving 11% of its dry weather flow from textile mills, could meet the discharge consent following the addition of 5 ppm Magnafloc 368 directly to the activated sludge tank and a concomitant halving of the effluent absorbance.\textsuperscript{53} In cases where higher polymer concentrations were necessary, however, severe problems with inhibition of nitrification were observed.\textsuperscript{17} The toxicity of polymers toward nitrifiers is highly variable, with IC\textsubscript{50} values ranging from 8 to >100 ppm.

Heathcoat & Co. Ltd (UK) discharges 2000 m\(^3\) day\(^{-1}\) from reactive dyeing and finishing operations. They achieve their direct discharge consent with a chemical pre-treatment using lime (pH 11-3), FeSO\(_4\), and polyelectrolyte followed by percolation through beds of expanded porous shales against a flow of air.\textsuperscript{70} Together with color, the physico-chemical pre-treatment removes anionic surfactants (but not the non-ionic ones). Many process chemicals, including several non-ionic surfactants and one complete range of dyestuffs, had to be replaced by more biocompatible ones.

Coagulation/flocculation, alone or in combination with biological processes, can sometimes allow water reuse. A production plant of Courtaulds Textile, the largest UK manufacturer of socks, has been using, since 1995, a full-scale purely physico-chemical process to treat the mixed effluent from their dyeing, printing and finishing units. The process consists of dye adsorption onto synthetic organic clays which are separated following the addition of alkali and a coagulant with high relative molecular mass. Even though cotton is the main fiber being processed, and thus reactive dyes the main dye class used; 50% water reuse is possible in the fiber being processed, and thus reactive dyes the main dye class used; 50% water reuse is possible in the
dyeing units.\textsuperscript{71} This new technology is being applied at several locations. Similarly, a leading denim conditioning and washing mill in Yorkshire recently built a full-scale flocculation plant. The effluent quality is consistently within the consent limit and half of it is reused.\textsuperscript{72} Finally, a textile processing plant located in Cyprus recycles its effluent (200 m\(^3\) day\(^{-1}\)) on irrigated land.\textsuperscript{51} Equalized wastewater is first treated with lime, FeSO\(_4\), and polyelectrolyte before entering the activated sludge tank which is equipped with anoxic selector in order to eliminate bulking. Tertiary treatment consists of disinfection with Cl\(_2\), flocculation with alum and polyelectrolyte, and finally filtration on anthracite, quartz sand and barytes. The final colorless effluent (5–18 nephelometric turbidity units) had a BOD\(_2\) and COD of 10 and 100–310 mg dm\(^{-3}\), respectively. Total operating costs amount to 0-2 US$ m\(^{-3}\).

While most coagulation/flocculation systems rely on lime, one laboratory study reported efficient color removal (90%) from spent reactive dyebath with 50 ppm Fe\(^{3+}\) or Al\(^{3+}\) under acid conditions.\textsuperscript{73} Final clarification allowed reuse of water and salt with no loss of fastness to light or washing.

### 3.4 Full-scale plants using ozonation

Ozone decolorizes all dyes, except non-soluble disperse and vat dyes which react slowly.\textsuperscript{74,78,79} Because O\(_3\) is less efficient with high-strength raw textile wastewater, it is advisable to use O\(_3\) only as a final treatment or at least following chemical coagulation.\textsuperscript{74,78,79} Aside from color, ozonation also removes a large proportion of AOX,\textsuperscript{80} surfactants,\textsuperscript{80} and organic substances.\textsuperscript{80} Typical ozonation products are dicarboxylic acids and aldehydes, which explains the little reduction of COD (0–20%) but substantial increase of BOD during ozonation.\textsuperscript{80,81}

Ozonation is becoming increasingly popular as a final treatment to eliminate color and other persistent substances. The sewage works at Leek receives 60% of its total load (76000 inhabitant equivalents) from seven dyehouses. Considerable extensions to the works were required following tighter discharge consent since 1992.\textsuperscript{5} Following pilot-scale investigations showing that required color removal could be achieved with 9.5 ppm O\(_3\) with an HRT of 20 min, a tertiary treatment involving lagoons, sand filters and an ozonation plant was built at a capital cost of £5 million. In about 1 year, only four samples out of 39 analyzed have failed the color consent. It is considered that O\(_3\) may be used on treated sewage effluent where the proportion of colored dyewaste to domestic sewage is high enough to justify the capital cost. In one case, the installation of an ozonator at a sewage works doubled the discharge levies bill to the textile companies, from £0.4 to £0.8 m\(^{-3}\).\textsuperscript{54}

The Alto Lura WWTP (Como, Italy) treats a mixture of 75% textile and 25% municipal wastewater with a sequence of pre-denitrification, activated sludge, sand filtration and ozonation. The ozonator was built in 1992 in order to reduce surfactants and color in the final effluent. These goals are being achieved with 20 mg O\(_3\) dm\(^{-3}\) but unwanted by-products are formed, especially aldehydes in the range 0.5–2 mg HCHO dm\(^{-3}\) (Bianchi, unpublished). Plans are made to reduce aldehyde formation by adding a tertiary flocculation unit before the sand filters (Fig. 1).

Numerous textile wet-processors also use ozonation in order to reuse the water. Capital costs are, however, high. A dyeing mill, producing 100 m\(^3\) h\(^{-1}\) wastewater, was recently built in Italy at a total cost of 13 million US$, of which 20% was allocated to the wastewater.
treatment plant (clarification, equalization, activated sludge, decanter, filtration, and ozonation). In the case of the above-mentioned silk and Lycra printing factory in Como, laboratory trials have demonstrated that up to 65% reuse, in washing and printing units, will be possible by integrating an ozonation reactor (20 mg dm$^{-3}$ O$_3$) which eliminates the residual color and non-ionic surfactants. The Levi Strauss finishing plant at Wervik, Belgium, was recently facing limitations in groundwater pumping and stringent discharge standards. Use of tap or river water was inadequate. Reuse trials in pilot plants with coagulation/flocculation or ultrafiltration showed deterioration of garment quality. Activated carbon filtration yielded a better COD and color removal and garment quality but sulfide formation in the filter yielded odor problems. Finally, a solution was found by treating the mixed stream with a sequence of coagulation/flocculation, activated sludge, and a 10-min final ozonation step (Fig. 1). Three years of pilot testing demonstrated the feasibility of 70% water reuse without deterioration of garment quality.

Numerous laboratory-scale experiments have documented the feasibility of ozonating dyebaths effluents separately and reusing the decolorized effluent several times with excellent color reproducibility. For example, spent reactive dyebath can be renovated and reused by coarse filtration followed by ozonation. Cost savings associated with the reuse of salts (80 g dm$^{-3}$ in reactive dyebaths) are up to 30 times larger than the savings associated with the reuse of water. Even though considerable amounts of O$_3$ (up to 1 g dm$^{-3}$) may be required to achieve nearly complete color removal due to high dye concentration (several hundreds ppm) and interference by dyeing auxiliaries, theoretical payback periods as short as 1-3 years are claimed. Reports on full-scale application of a reuse strategy involving separate ozonation of dyeabath effluents are, however, apparently lacking. The reason could be the sometimes considerably lower decolorization rate, up to 20 times, in the presence of dyeabath additives such as EDTA, silicone defoamers, ethoxylated alcohol surfactants, leveling agents, butyl benzate carriers, guar gum and salts. As a consequence, the amount of O$_3$ necessary for near complete decolorization may become prohibitively expensive.

### 3.5 Full-scale plants using filtration processes

Ultrafiltration, nanofiltration and reverse osmosis have been used for the full-scale treatment and reuse of water and chemicals by South African textile wet processors for nearly two decades. Specific filter configurations have been developed for the reuse of wool scour and bleaching effluents, spent sizing and desizing liquors, and spent dyebaths. The high cost of filtration techniques may be outweighed by the significant costs savings achieved through the reuse of permeate, salts and sizes (i.e., polymers applied to warp yarns to facilitate weaving). While careful choice of the membrane system, use of pre-filters and regular cleaning eliminate membrane fouling problems, economic viability of concentrated waste treatment and disposal remains uncertain. In South Africa, where filtration techniques are widely used in order to reuse water, the concentrates are often dumped in the ocean or disposed to a sewer.

Desizing effluents typically contain 25-50% of the total organic load in 5-10% of total effluent volume. As early as 1978, UF was used commercially to recover polyvinyl alcohol sizes from desizing effluents. Both the retained sizes and the permeate are reused. Polyacrylate sizes were also successfully recovered and reused from desizing effluents using high temperature UF pilot plants. Hot permeate reuse yields savings in heat and water.

Wool scouring liquors can also be treated by filtration techniques. Norway's largest yarn factory generates hot wool scouring liquors containing high pH detergents and up to 100 g COD dm$^{-3}$. A full-scale ultrafiltration treatment plant has been operating since 1989 with > 80% removal of COD, fats and suspended solids. The permeate is disposed to a sewer and the concentrate (10% v/v) must be trucked to lagoons at high cost. Membrane lifetime is 1 year with an average flow of 60 dm$^3$ m$^{-2}$ h$^{-1}$. AOX, of which 50% are in solid form in wool effluent, are also significantly reduced by filtration techniques. Wool scouring liquors are also being reused in full-scale plants using dynamic UF membranes. The latter offer the advantage of not requiring membrane replacement since it is formed in situ by deposition of a colloidal suspension of hydrated zirconium oxide on a porous support. The membranes, which are reformed every other month, achieve up to 90% TS rejection and allow 85% water recovery.

Dyehouse effluents are also being reused successfully following reverse osmosis. In this case, only water reuse is possible. Coagulation and microfiltration are necessary to prevent membrane fouling. Treffry-Goatley et al. reported the successful treatment and reuse of dyehouse effluents in a pilot plant (50 m$^3$ day$^{-1}$) integrating the sequence of alum coagulation, microfiltration and reverse osmosis. Concentrate volume was only 5-10% and RO membrane lifespan 2 years. Similarly, Buckley reports on a pilot coagulation-microfiltration-RO sequence treating 40 m$^3$ day$^{-1}$ of cotton/polyester dyehouse effluent. A UF plant equipped with dynamic membranes has been achieving, since 1985, 85% water recovery with 80% ionic rejection and 95% color rejection at a textile mill dyeing polyester/viscose fibers. The application of filtration technologies remains, however, severely limited.
by the problem of disposal of the concentrate stream since the currently-used schemes, such as evaporation or ocean discharge, are either economically or environmentally unacceptable.

Because dyebath salts may have a 10-fold greater value than water, it may be preferable to treat and reuse dyebath and rinse effluents separately with membranes that let pass the salts but retain the dyes. Such a reuse strategy is described by Erslew et al. for a South African cotton dyehouse. In this case, a charged UF membrane was used for dyebath effluents that allowed 90% reuse of salt and water, while a 10% (v/v) concentrate was disposed of. The volume of the concentrate stream was reduced to only 2% in an elegant reuse scheme described by Woerner et al. in the case of a cotton mill (160 tons per month). Reuse of permeate with electrolytes yielded a payback period of less than 3 years. The rinse liquors are reused following a sequence of UF and RO. The concentrate is mixed with the dyebath effluent which is subjected to the sequence UF and NF enabling both water and electrolytes reuse. Buckley reports on an NF plant treating reactive dye liquors from a cotton dyehouse (200 tons per month). Reuse of permeate with electrolytes yielded a payback period of less than 3 years. Even microfiltration has been used in the case of polyester dyebaths using insoluble disperse dyes. The slight residual color in the permeate did not prejudice its reuse in dyeing or rinsing units.

### 3.6 Full-scale plants using the Fenton’s reagent (H₂O₂ + ferrous iron)

Several full-scale Fenton’s reagent plants were built recently in South Africa to treat textile mill effluents. This technology is effective in decolorizing a wide range of dyes. According to Lin and Peng, the Fenton’s reagent works by oxidizing ferrous to ferric iron with simultaneous splitting of H₂O₂ into hydroxide ion and hydroxyl radical. The latter oxidizes the dye while the former precipitates with ferric iron together with organics. The reagent is used preferably at pH values around 3-4. Ferrie seems as effective as ferrous iron, and only a few ppm are required if high temperatures are used. For example, 1 g dm⁻³ of a direct dye was completely decolorized in 30 min with 1.5 g dm⁻³ of H₂O₂ in the presence of 2 mg dm⁻³ Fe at 98°C. At normal temperatures, 50–100 mg Fe²⁺ dm⁻³ are required. Lin and Peng obtained very good performance in a pilot scale installation treating actual textile wastewaters with the sequence of chemical precipitation, Fenton’s reagent and activated sludge. Complete decolorization was obtained after the Fenton’s reagent stage and final COD, after activated sludge, was only 80 mg dm⁻³. Estimated total running costs, not including sludge disposal, was 0.4 US $ m⁻³ which was cheaper than that of the conventional treatment.

### 4 EMERGING TECHNOLOGIES AWAITING FULL-SCALE TRIALS

#### 4.1 Electrolysis

Through Fe(OH)₂ production with sacrificial iron electrodes, electrolysis can be used to remove acid dyes very effectively via sorption onto the precipitated iron and via Fe(II)-driven reduction of azo dyes to amines. Solutions containing 50 mg dm⁻³ dyes were 100% decolorized with 100–150 mg Fe dm⁻³. Greater than 80% decolorization of a real textile effluent was achieved in laboratory-scale trials by applying 2 kWh/m⁻³. The process was used very successfully by Lin and Peng in a pilot scale installation treating the raw effluent from a cotton/polyester dyeing and finishing mill in Taiwan. The effluent, which contained 15 different dyes and 800–1600 mg COD dm⁻³, was fully decolorized in an electrolyte cell (HRT = 18 min) with a concomitant 50% COD reduction. The total process, consisting of coagulation–electrolysis–activated sludge, was cheaper (running costs, not including sludge disposal, was 0.3 US $ m⁻³) and more effective (COD in final effluent = 80 mg dm⁻³) than the conventional treatment. Other pilot-scale trials have proven equally successful.

#### 4.2 Photocatalysis

UV light has been tested in combination with H₂O₂ or solid catalysts such as TiO₂ for the decolorization of dye solutions. While the UV/H₂O₂ process appeared too slow, costly and little effective for potential full-scale application, the combination UV/TiO₂ seems more promising. Because UV penetration in dye solutions is an inherent limitation, Huang et al. found the best use of UV technology as a post-treatment after ozonation. Not only was the residual color completely removed, close to 90% of residual total organic carbon was also removed from the effluents of two textile mills. The German firm Wedeco is using such a combination of O₃/UV/H₂O₂ in a mobile pilot plant.

#### 4.3 Sorption

Despite the fact that effective decolorization has often been shown to be feasible via sorption onto activated carbon as a final step, full-scale use of this technology has apparently not been reported yet, a likely consequence of high capital and regeneration costs and possible foul odors. CIDA Srl is currently testing full-scale GAC filters at the Alto Lura WWTP (Fig. 1) as part of the research project supporting this
paper. The final effluent seems suitable for reuse in silk desizing units but not in silk dyeing units. Full-scale biologically-activated GAC filters are also under investigation at the site. Though certain microbial species may sorb impressive quantities of dyes (up to 3 g sulfur at the site. Though certain microbial species may sorb impressive quantities of dyes (up to 3 g sulfur tigation at the site. Though certain microbial species biologically-activated GAC filters are also under inves- desizing units but not in silk dyeing units. Full-scale paper. The final effluent seems suitable for reuse in silk Ñyash or biogas residual slurry were disap- pointed.111–114 Lazlo115 reviewed the effectiveness of all biological adsorbents for removing anionic dyes. The highest affinity adsorbent was cross-linked chitosan at a pH of 3–4. The best choice was quaternized lignocellu- losic biomass which offers the advantages of high sorption capacity, low cost, rapid kinetics and possible regeneration.

4.4 Flotation and others

Lin and Lo116 demonstrated the potential of foam flota- tion as an effective and simple technology for the decolorization of dyehouse effluents. Mixing the waste- water with 70 mg dm$^{-3}$ of a surfactant and compressed air yielded, after a few minutes, 90% color removal and 40% COD removal. Color and COD were recovered in a highly concentrated stream after the foam, leaving the contact chamber at the top, had passed through a foam breaker. Solvent extraction can also be applied for dye recovery from dyebath effluents. For example, sul- fonated dyes can be rendered hydrophobic with long chain amines at pH 2.5 and concentrated up to 1000- fold in a solvent phase.16 Dyes, solvent and surfactants are reused.

*Phanerochate chrysosporium* and other fungal species can mineralize all types of dyes at a very rapid pace via a peroxidation pathway.43,117,118 Van der Waarde *et al.*119 developed a decolorization technique based on the combined use of fungal degradation and *in situ* electrochemical H$_2$O$_2$ production, an essential substrate for fungal activity. They achieved complete decolorization of several spent dye liquids (reactive and disperse dyes) in an air lift continuous reactor.

At 150–250°C and partial O$_2$ pressures of 0.35–1.4 MPa, concentrated solutions of dyes are fully decolorized and almost completely mineralized in 1–4 h.120 Because no external energy is required when the COD exceeds 20 g dm$^{-3}$, wet air oxidation may offer a solution for the problematic disposal of the concentrate streams produced by filtration or foam flotation tech- nologies.

5 CONCLUSIONS

Conventional WWTP relying on activated sludge systems are not adequate for the treatment of textile mill effluents, neither on site nor after dilution with domestic wastewater at the sewage works. Activated sludge and other types of bioreactor fail to remove sufficient color, COD, N, surfactants and other micro- pollutants present in the textile effluents. Tertiary coagulation/flocculation is often used with variable results but at times near-complete decolorization and water reuse is possible; sludge disposal remains, however, a problem. Ozone is increasingly used as a final step but cost and aldehyde formation prevent its wider acceptance. Membrane filtration of process sub- streams may yield substantial cost savings by allowing water, chemicals and heat reuse. Handling and disposal of the concentrate stream remains, however, a severe limitation to filtration processes. In view of the need for a technically- and economically-satisfying treatment technology, a flurry of emerging technologies are being proposed and tested at different stages of commer- cialization. Promising among these are biologically-activated GAC filtration, foam flotation, electrolysis, photocatalysis, (bio)sorption and Fenton oxidation.

Broader validation of these new technologies and inte- gration in the current treatment schemes will, most likely in the near future, render these both efficient and economically viable.

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