FS-AVA-001

ADVANCED OXIDATION PROCESSES (AOPs)

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INDITEX

ADVANCED OXIDATION PROCESSES (FS-AVA-001)

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1.- INTRODUCTION

Advanced oxidation processes (AOPs) are defined as "those oxidation processes involving the generation of hydroxyl radicals in sufficient quantity to interact with the organic compounds the average amount". This is a family of methods that use the high capacity of oxidizing radicals HO^- and which differ in the way they are generated. The most common use combinations of ozone (O_3), hydrogen peroxide (H_2O_2), ultraviolet radiation and catalysis. A relationship is indicated in the following table. A consequence of the high reactivity of the oxidizing agent is that advanced oxidation processes are also characterized by their low selectivity; but which in a production process can be a disadvantage, however, is a desirable characteristic in the case of removing grouped pollutants (BOD, COD, colour,…) from wastewaters.

Table 1.- Advanced oxidation processes (AOPs) (Adapted from Rodríguez et al., 2006)

Homogeneus processes	
No external power supply	Ozonation in alkaline medium (O_3/OH^-) Ozonation with hydrogen peroxide (O_3/H_2O_2) y ($O_3/H_2O_2/OH^-$) Catalyst and hydrogen peroxide (H_2O_2/Fe^{2+})

With external energy input	Energy from ultraviolet radiation (UV)
	     Ozonation and UV radiation (O_3/UV)
	     Hydrogen peroxide and ultraviolet radiation (H_2O_2/UV)
	     Ozone, hydrogen peroxide and ultraviolet radiation ($O_3/H_2O_2/UV$)
	     Photo-Fenton ($Fe^{2+}/H_2O_2/UV$)
	 Energy from ultrasounds (US) (Sonolysis)
	     Ozonation and ultrasounds (O_3/US)
	     Hydrogen peroxide and ultrasound (H_2O_2/US)
	 Electrochemistry
	     Electrochemical oxidation
	     Anodic oxidation
	     Electro-Fenton

Heterogeneous processes	
	Catalytic ozonation ($O_3/Cat.$) Photo catalytic ozonation ($O_3/TiO_2/UV$) Heterogeneous photo-catalysis ($H_2O_2/TiO_2/UV$)

One AOPs characteristic is that its ability to treat wastewater flows is limited to a concentration of chemical oxygen demand (COD) of less than 5000 mg/L (Rodriguez et al., 2006). At greater concentrations, the high oxidant consumption and improvement in the energy balance of the process, make preferable direct oxidation techniques such as wet oxidation. Another feature of the AOPs, is that in the case of waste water from the textile industry, its application is very oriented color reduction (Edwards, 2000).

1.1.- Particular case of the use of chlorine as an oxidizing dye

In the above table chlorine compounds do not appear from oxidizing products. But, the chlorination (using chlorine gas or sodium hypochlorite, i.e. NaOCl) has been evaluated for its effectiveness in colour removal. The conclusions of several authors do not allow a clear approach in this regard. Chlorine is reported to be more effective for dye decolourization at pH 3.5 than at pH 7.0 or 10.0. Chlorine rapidly decolourized acid and reactive dye but even large doses of chlorine failed to completely decolorize direct and disperse dyes (Joshi et al., 2004).

Although, decolourization using sodium hypochlorite is inexpensive and effective but dechlorination of wastewater is necessary in order to prevent toxic effects in the ensuing biological processes. Moreover, chlorine is viewed with increasing disfavour because it has potential for generating toxic chlorinated compounds i.e. AOX (absorbable organohalides) that are harmful to humans and environment Joshi et al., 2004).

Chlorine dioxide is less reactive tan chlorine and has been claimed to give rise to fewer side reactions. Chlorine dioxide exists as a stable, nonmetallic, monomeric free radical and is highly soluble in water. Because it does not hydrolyse in water, ClO_2 exists as a dissolved gas as long as the pH remains between 2 and 10. Once the ClO_2 has reacted with organic matter, chlorite (ClO_2^-) and chlorate (ClO_3^-) by-products are formed (Edwards, 2000).The experimental studies show, however, that it does not decolorize dye waste efficiently to consent conditions, as it has no effect on some dye classes, such as vat dyes. Nevertheless, chlorine dioxide is highly effective against reactive, direct, disperse and ionic premetallised dyes. It could be used as a polishing treatment (Joshi et al., 2014).

Chlorine dioxide and hypochlorite do not show satisfactorily results for textile wastewater treatment (Abdul-Aziz et al. 2014). That is why; these oxidizing agents are not preferable for textile wastewater treatment as this process cannot help to achieve desired discharge standards. However, hypochlorite and chlorine dioxide can possibility be used in combination with conventional methods. The residual chlorine has the disadvantage of generating toxic organochloride compounds, hazardous to the environment and public health. The use of chlorine for dye removal is becoming less frequent due to the negative effects it has when released into waterways and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules (Robinson et al. 2001).

1.2.- AOPs for textile wastewater treatment

Major pollutants specifically found in textile wastewater are suspended solids, highly recalcitrant chemical oxygen demand, dyes giving intense colour and other soluble substances. The removal of colour from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern. Its strongest impact on the environment is related to primary water consumption (80–100 m^3/ton of finished textile) and wastewater discharge (115–175 kg of COD/ton of finished textile, a large range of organic chemicals, low biodegradability, colour, and salinity) (Savin and Butnaru 2008). Therefore, reuse of the effluents represents an economic and ecological challenge for the entire sector. Textile processing employs a variety of chemicals, depending on the nature of the raw material and product (Aslam et al., 2004). The effluents resulting from these processes differ greatly in composition, due to differences in processes, fabrics and machinery.

Typical textile industry wastewater characteristics can be summarized by a COD range from 150 to 12000 mg/L, total suspended solids between 2900 and 3100 mg/L, total Kjeldahl nitrogen from 70 to 80 mg/L, and BOD range from 80 to 6000 mg/L leading to a BOD/COD ratio of around 0.25, showing that it contains large amounts of nonbiodegradable organic matter. An important group of auxiliary textile chemicals are non-ionic (ethoxylate) + anionic (aryl sulfonate) detergent mixtures that are frequently applied in the preparation (scouring, washing and mercerizing) stage to remove impurities from the fabric and prepare them for dyeing.

Research studies in this field have usually focused on the development of new treatment strategies for synthetic wastewater mainly containing azo-dyes, the largest class of dyes used in textile industry, and surfactants, which are responsible for foam formation on the surface of rivers, anomalies in the growth of algae (eutrophication) and toxicity for some aquatic organisms. Furthermore, few studies have been carried out using synthetic textile wastewater or real wastewater coming from the different steps in textile manufacturing. In this sense, AOPs have been widely shown to have the greatest promise for treating textile wastewater as summarized in Table 2.

Table 2.- A brief summary of research studies in which AOPs were used for treating textile or dyeing wastewater (Adapted from Oller et al., 2011)

Advanced Oxidation Processes	Concluding remarks
Conventional chemical treatment methods: $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3$ and $FeSO_4$ compared to AOPs (O_3, O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, Fe^{2+}/H_2O_2)	Superior performance of O_3/H_2O_2/UV system: 99% COD removal and 96% colour removal from a fibre dyeing effluent.
O_3/H_2O_2/UV, H_2O_2/UV	Effectively decolourized dyes and synthetic textile wastewater (COD removed was not complete).
Ozonation	Formation of by-products which increased toxicity of the formulation.
TiO_2-assisted photocatalysis. Ozonation.	Complete decolourization and TOC reduction over 60%. 60% decolourization and negligible TOC reduction.
TiO_2 photocatalysis (solar light or UV) with or without H_2O_2	High removal efficiency for reactive dyes.
Photocatalytic membrane reactor (PMR) integrating novel flat plate PTFE membrane module along with a TiO_2 slurry photo-reactor	Nearly 99.99% colour removal and 75–85% TOC and COD removal. Faster than an anaerobic (aerobic membrane biological process for the mineralization of Reactive Black 5 dye.
Fenton and photo-Fenton (solar light or UV)	Successful treatment of textile dyes and commercial surfactants.
Electrochemical and electro-Fenton (Fe^{2+} in combination with electro-generated H_2O_2 on the polyacrylonitrile-based activated carbon fibre cloth cathode)	Successful treatment of textile effluents and real dyeing wastewater.

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1.3.- About of colour as important problem of textile wastewater

The textile industry is very water intensive. Water is used for cleaning the raw material and for many flushing steps throughout production. Textile wastewater includes additions of a wide variety of dyes and chemicals that make the chemical composition of textile industry effluents an environmental challenge. Textile industry dyes are intentionally designed to remain photolytically, chemically and biochemically stable, and thus are usually not amenable to biodegradation (Yonar, 2010). Most pollution in textile wastewater comes from dyeing and finishing processes. Textile finishing includes bleaching, dyeing, printing and stiffening during processing of textile products. The textile industry's impact on the environment, both in terms of the discharge of pollutants and of the consumption of water and energy, has been recognized for some time.

Another important problem of textile industry wastewater is color. Without proper treatment of colored water, these dyes may remain in the environment for a long time (Yonar et al, 2005). The problem of colored effluent has been a major challenge and an integral part of textile effluent treatment as a result of stricter environmental regulations. The presence of dyes in receiving media is easily detectable even when released in small concentrations. This is not only unsightly but dyes in the effluent may have a serious inhibitory effect on aquatic ecosystems (Nigam et al., 2000).

Definition and determination of colour is another important point for most water and wastewater samples. Some methods can be found in literature for the determination of colour in samples. But, selection of true method for the determination of colour is very important. According to "Standard Methods for the Examination of Water and Wastewater" (APHA 2000), importance of colour is defined with some sentences given below: "Colour in water may result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. Colour is removed to make water suitable for general and industrial applications. Colored industrial wastewaters may require colour removal before discharge into watercourses." From these reasons, colour content should be determined carefully. In Standard Methods, colour content of water and wastewater samples can be determined with four different methods such as (i) Visual Comparison Method, (ii) Spectrometric Method, (iii) Tristimulus Filter Method, and (iv) ADMI Tristimulus Filter Method. Selection of true and appropriate method for samples is very important. Visual comparison method is suitable for nearly all samples of potable water. This method is also known as Platinum/Cobalt method. Pollution by certain industrial wastes may produce unusual colour that cannot be easily matched. In this case, usage of instrumental methods is appropriate for most cases. A modification of the spectrometric and tristimulus methods allows calculation of a single colour value representing uniform chromaticity differences even when the sample exhibits colour significantly different from that of platinum cobalt standards (APHA 2000).

1.4.- AOPs need to combine with other processes

AOPs use expensive reagents such as hydrogen peroxide or ozone, or consume large amounts of energy (UV, etc.). It has been found that their potential is achieved when integrated or complemented by other processes such as adsorption or biological processes in order to achieve maximum economy efficiency of oxidant and/or energy (Rodríguez et al., 2006; Sala et al., 2014).

Due to their synthetic origin and complex structure deriving from the use of different chromophoric groups, dyes are extremely recalcitrant. Along with the recalcitrant nature of dye wastewater, the frequent daily variability of characteristics of such wastewater adds to the difficulty of treatment. Accordingly, despite the fact that virtually all the known physicochemical and biological techniques have been explored for decolourization, none has emerged as a panacea. Cost-competitive biological options are rather ineffective, while physicochemical processes are restricted in scale of operation and pollution profile of the effluent. Table 3 lists the advantages and disadvantages of different individual techniques.

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Table 3.- Advantages and shortcoming of the current methods of dye removal from industrial wastewater (Adapted from Robinson et al., 2001; Hai et al., 2007)

Process	Advantages	Disadvantages
Advanced oxidation processes, AOPs	Generate a large number of highly reactive free radicals and by far surpass the conventional oxidants in decolourization.	AOPs in general may produce further undesirable toxic by-products and complete mineralization may not be possible. Presences of radical scavengers reduce efficiency of the processes some of which are pH dependent. Cost-prohibitive at their present stage of development.
UV/O_3	Applied in gaseous state, no alteration of volume. Good removal of almost all types of dyes; especially suitable for reactive dyes. Involves no sludge formation, necessitates short reaction times.	Removal is pH dependent (neutral to slightly alkaline); poor removal of disperse dyes. Problematic handling, impose additional loading of water with ozone. Negligible or no COD removal. High cost of generation coupled with very short half-life and gas-liquid mass transfer limitation; suffers from UV light penetration limitation. Increased level of turbidity in effluents.
UV/H_2O_2	Involves no sludge formation, necessitates short reaction times and reduction of COD to some extent may be possible.	Not applicable for all dye types, requires separation of suspended solid and suffers from UV light penetration limitation. Lower pH required to nullify effect of radical scavengers.
Fenton reagent	Effective decolourization of both soluble and insoluble dyes; applicable even with high suspended solid concentration. Simple equipment and easy implementation. Reduction of COD (except with reactive dyes) possible.	Effective within narrow pH range of <3.5; and involves sludge generation. Comparatively longer reaction time required. Sludge generation.
Ozonation	Applied in gaseous state: no alteration of volume.	Short half-life (20 min).
Photocatalysis	No sludge production, considerable reduction of COD, potential of solar light utilization.	Light penetration limitation, fouling of catalysts, and problem of fine catalyst separation from the treated liquid (slurry reactors).
Electrochemical	Effective decolourization of soluble/insoluble dyes; reduction of COD possible. Not affected by presence of salt in wastewater. Breakdown compounds are non-hazardous.	Sludge production and secondary pollution (from chlorinated organics, heavy metals) are associated with electrocoagulation and indirect oxidation, respectively. Direct anodic oxidation requires further development for industrial acceptance. High cost of electricity is an impediment. Efficiency depends on dye nature.
Photochemical	No sludge production.	Formation of by-products.
Sonolysis	Addition of chemical additives not required and hence does not produce excess sludge.	Requires a lot of dissolved gas (O_2); complete decolouration and mineralization by sonification alone are not economical at present level of reactor development.
Ionizing radiation	No sludge production; effective oxidation at lab scale.	Requires a lot of dissolved O_2; complete decolouration and mineralization by stand-alone application not possible. Energy efficient scale-up yet to be achieved.
Wet air oxidation, WAO	Well-established technology especially suitable for effluent too dilute for incineration and too toxic and/or concentrated for biological treatment.	Complete mineralization not achieved, as lower molecular weight compounds are not amenable to WAO. High capital and operating costs are associated with elevated pressure and temperature employed.

It can be concluded that a single, universally applicable end-of-pipe solution is unrealistic, and combination of different techniques is required to devise a technically and economically feasible option. Hai et al. (2007) recently published a comprehensive review of potential hybrid technologies found in the literature for treatment of dye wastewater in general and textile wastewater in particular. Based on the array of potential hybrid technologies and the available cost information, it can be concluded that biological hybrid technologies appear to be the most promising.

In these integrated processes, in contrast to the conventional pre- or post-treatment concepts, where process designs of different components are independent of each other, the effectiveness of combining biological and other treatments is specifically designed to be synergetic rather than additive.

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Although still mostly in laboratory stage of development, of late, a wealth of studies have been reported on implementation of advanced oxidation processes (AOPs) and their combinations for dye wastewater treatment. Many studies have focused on different combinations of physicochemical treatments, which often have been employed by industries in simple, standalone manner. Combinations of conventional physicochemical techniques with the AOPs have also appeared as attractive options. The biological systems, in addition to varieties of combinations among themselves, have also been explored in fusion with virtually all sorts of physicochemical and advanced oxidation processes.

The combinations have been outlined under three broad categories: combination among AOPs, combination of physicochemical treatments among themselves and those with the AOPs, and, with paramount importance, the combination of biological systems with conventional physicochemical processes and AOPs. Before elaborating on the combinations, the basic principles and limitations of relevant individual techniques are discussed briefly. Based on the array of potential hybrid technologies and the available cost information, a conceptual on-site textile dye wastewater treatment system integrated with energy and water recovery/reuse has been proposed.

2.- COMBINATION AMONG AOPs

While advanced oxidation processes (AOPs) have been studied extensively both for recalcitrant wastewater in general and dye wastewater in particular, their commercialization has yet not been realized because of prevailing barriers. These processes are cost prohibitive and complex at the present level of their development. Additional impediment exists in treatment of dye wastewater with relatively higher concentration of dyes, as AOPs are only effective for wastewater with very low concentrations of organic dyes. Thus, significant dilution is necessary as a facility requirement. The presence of dye additives/impurities such as synthetic precursors, by-products, salts, and dispersing agents in commercial dye bath recipe causes further reduction in process efficiency. Although the usual small-scale laboratory investigations reveal encouraging results, such studies are insufficient to cast light on practical feasibility of AOPs. For example, in photochemical/photocatalytic decolouration, most of the investigations involve reactors ranging from as small as few tens of millilitres (e.g., 40 ml) to several hundreds of millilitres (e.g., 250 ml) or at best few liters (e.g., 4 L), which are inadequate to explicitly address the light penetration issue, the inherent drawback of this technology (Hai et al., 2006). Only a handful of pilot plant explorations with less than persuasive or moderate results have been documented. Reports on full-scale application of sole AOP treatment of dye bath effluents are apparently lacking. Nevertheless, such processes generate a large number of highly reactive free radicals and by far surpass the conventional oxidants in decolourization.

The conventional oxidants have more significant thermodynamic and kinetic limitations. For the AOPs, the basic reaction mechanism is the generation of free radicals and subsequent attack by these on the pollutant organic species. Hence it is strongly believed that their combination will result in more free radicals, thereby increasing the rates of reactions. Moreover, some of the drawbacks of the individual AOPs may be eliminated by the characteristics of other AOPs. The cost/energy efficiency, however, will be dependent on the operating conditions and the type of the effluent. Tables 4-6 furnish a quasi-exhaustive list of typical examples of studies on combinations among AOPs for dye wastewater treatment. Information on type of associated dyes has been included wherever available.

Different Photochemical Processes

The photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the chemical species present in the solution. Generation of radicals through ultraviolet (UV) radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide, ozone, or Fenton's reagent has been frequently reported to be superior to solely UV radiation or sole utilization of such oxidants. Highly UV absorbing dye wastewater may inhibit process efficiency by limiting penetration of UV radiation, necessitating use of high-intensity UV lamps and/or a specifically designed reactor. One example of an appropriate reactor is a reactor that generates internal liquor flow currents bringing all liquor components into close proximity to the UV source. Conversely, a thin-channel coiled reactor may also be used. Arslan and Balcioglu (2001) proposed pre-ozonation to remove high UV-absorbing components, and thereby to accelerate subsequent H_2O_2–UV treatment by increasing UV penetration. Simultaneous use of $UV/H_2O_2/O_3$ has also been reported to yield enhanced reaction kinetics. However, this entailed additional cost as compared to UV/H_2O_2 or UV/O_3, and hence such use is recommended to be weighed against degree of removal required and associated cost. As activators of oxidants like O_3 or H_2O_2, a handful of studies have put forward other alternatives to UV, namely, reduced transition metals, gamma irradiation, humic substances, etc. An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors, that is, heterogeneous photocatalysis.
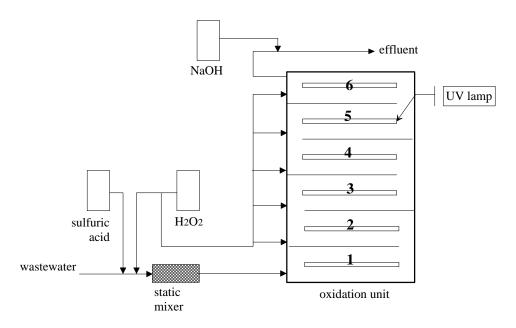
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Figure 1.- Flow configuration in a UV/H₂O₂ system (Adapted from USEPA 1998)
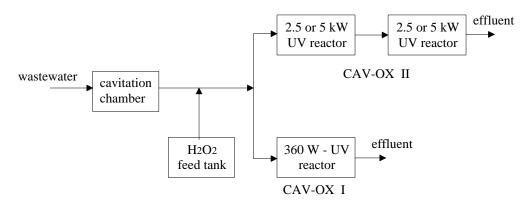

Figure 2.- Flow configuration in a CAV-OX® UV/H₂O₂ system (Adapted from USEPA 1998)

Various chalcogenides (oxides such as TiO_2, ZnO, ZrO_2, CeO_2, etc. or sulfides such as CdS, ZnS, etc.) have been used as photocatalysts so far in different studies. However, titanium dioxide (TiO_2) in the anatase form is the most commonly used photocatalyst, as it has reasonable photoactivity. Moreover, it also furnishes the advantages of being insoluble, comparatively inexpensive, and nontoxic, together with having resistance to photocorrosion and biological immunity. The photocatalytic process can be carried out by simply using slurry of the fine catalyst particles dispersed in the liquid phase in a reactor or by using supported/immobilized catalysts. Limitations of slurry reactors are low irradiation efficiency due to the opacity of the slurry, fouling of the surface of the radiation source due to the decomposition of the catalyst particles, and the requirement that the ultrafine catalyst to be separated from the treated liquid. On the other hand, drawbacks of supported photocatalysis are scouring of films comprising immobilized powders of catalyst and reduced catalyst area to volume ratio. Recently fluidized bed reactors have been reported to take advantages of better use of light, ease of temperature control, and good contact between target compound and photocatalysts over slurry reactors or fixed bed reactors. Besides sole photocatalysis, reports on utilization of photocatalysis in presence of O_3 or H_2O_2, exhibiting enhanced decoloration and mineralization, are also available. Considering the total mineralization of the compounds, the photocatalytic ozonation ($UV/O_3/TiO_2$) may show much lower specific energy consumption than the conventional photocatalysis (UV/TiO_2) and ozonation ($UV/H_2O_2/O_3$).

Fenton reagent (a mixture of H_2O_2 and Fe^{2+}) and its modifications such as the thermal Fenton process or the photo-Fenton reaction using Fe(II)/Fe(III) oxalate ion, H_2O_2, and UV light have received great attention as means for decolourization of synthetic dyes. In the case of the photo-Fenton technique, H_2O_2 is utilized more rapidly by three simultaneous reactions, namely, direct Fenton action, photoreduction of Fe(III) ions to Fe(II), and H_2O_2 photolysis. Thus this process produces more hydroxyl radicals in comparison to the conventional Fenton method or to photolysis. Certain reports suggest that in case of similar removal performance, Fenton's process may be preferred

to related advanced oxidation alternatives (e.g., UV/H_2O_2) in view of lower energy consumption, lower H_2O_2 consumption, lower sludge disposal cost (as compared to higher reagent cost), higher flexibility, and lower maintenance requirement. However, Fenton reagent necessitates use of a large amount of acidic and alkaline chemicals (ideal pH about 2.5). Compared to Fenton's reagent, the β-FeOOH-catalyzed H_2O_2 oxidation process takes advantage of its applicability over a wider pH range between 4 and 8, and moreover no sludge is produced. In order to take advantage of the oxidizing power of Fenton's reagent yet eliminate the separation of iron salts from the solution, the use of an "H_2O_2/iron powder" system has been recommended. Such process may yield better dye removal than "H_2O_2/Fe^{+2}" due to the chemisorption on iron powder in addition to the usual Fenton-type reaction. Fenton-type reactions based on other transition metals (e.g., copper), although less explored to date, have also been reported to be insensitive to pH and effective for degradation of synthetic dyes. Among the AOPs, the photo-Fenton reaction and the TiO_2-mediated heterogeneous photocatalytic treatment processes are capable of absorbing near-UV spectral region to initiate radical reactions. Their application would practically eliminate major operating costs when solar radiation is employed instead of artificial UV light. The ferrioxalate solution that has long been being used as chemical actinometer may be used in photo-Fenton process to derive further benefit by replacing UV with solar radiation. Recently, several attempts have been made to increase the photocatalytic efficiency of TiO_2; these include noble metal deposition, ion doping, addition of inorganic coadsorbent, coupling of catalysts, use of nanoporous films, and so on. Apart from that, new catalysts, such as polymeric metalloporphyrins, have been reported to be easily excited by violet or visible light, whereas available utilization of solar energy by commonly used TiO_2 is only about 3%.
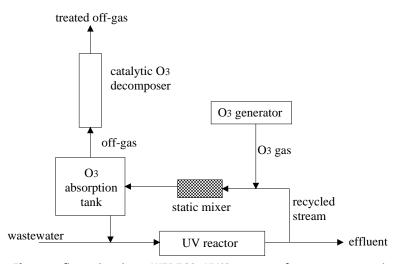

Figure 3.- Flow configuration in a WEDECO UV/O₃ system for water contaminated with chlorinated VOCs (Adapted from USEPA 1998)
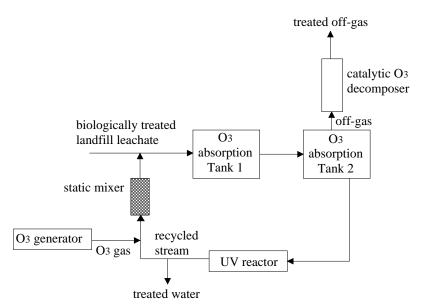

Figure 4.- Flow configuration in a WEDECO UV/O₃ system for biologically treated landfill leachate (Adapted from USEPA 1998)

Table 4.- List of typical examples of combinations among AOPs for dye wastewater treatment (Adapted from Hai et al., 2007)

Technology	Dye/wastewater	Details
UV/O$_3$	2-naphthalenesulfonate [Azo Dye intermediate]	Mineralization of 2-NS via ozonation (40 mg/L) is remarkably enhanced by UV radiation (60.35 W/m^2, 254 nm), tripling the rate. Not much.
UV/O$_3$, UV/H$_2$O$_2$	AcidN=N - red 1/black 1/red14/red 18/orange 10/yellow 17/yellow 23; DirectN=N yellow 4	Decolouration (20 mg/L dye): 100% in 10 min by O$_3$ (6 L/min O$_2$) with/without UV; 80% in 25 min by H2O2–UV. Negligible enhancement of ozonation by UV (low power) due to absorption of most UV by dye. Dilution of sample and/or optimum reactor design recommended.
UV/H$_2$O$_2$	Hispamin Black CA [DirectN=N Black 22]	UV (125 W)- H2O2 (565.8 mg/L, 16.6 mM): Complete decolouration (35 min) & 82% TOC removal (60 min) for 40 mg/L dye at natural pH (7.5), although subsequent toxicity test recommended.
UV/H$_2$O$_2$	Acid dye [orange 8N=N/blue 74C=C, Methyl orangeN=N]	Removal by Only UV (15 W, 253.7 nm, incident photon flux = 6.1×10^{-6} Einstein s^{-1}, $4.54 \leq$ pH ≤ 5.5) and only H$_2$O$_2$ in absence of UV was negligible. Combined: Decolourization rate rises by increasing the initial dosage of H$_2$O$_2$ up to a critical value ([H$_2$O$_2$]/ [dye] = 50–70) beyond which it is inhibited.
UV/H$_2$O$_2$	Reactive- red 120N=N /black5N=N /yellow 84N=N	UV (15 W)/H$_2$O$_2$ (optimum dose 24.5 mmol/l): 15 min: [Decolourization >65%, COD removal = 40–70%], 60 min: [Decolourization > 99%]; Degradation by products unobjectionable.
UV/H$_2$O$_2$ and solar/H$_2$O$_2$	Chlorotriazine ReactiveN=N Orange 4	Dye removal (0.5 mmol/L), 150 min, pH 3: UV (64W, 365 nm)-H2O2 (10 mmol) = 88.68% decolourization, 59.85% degradation. Sunlight–H$_2$O$_2$ = 80.15% decolourization, 50.91% degradation. Dye auxiliaries like Na$_2$CO$_3$, NaOH seriously retard decolouration rate while NaCl does not.
O$_3$ followed by UV/H$_2$O$_2$	Wastewater from cotton & polyester fibre dyeing textile mill	Under natural pH (10.66) 5 min preozonation (293 mg/L), removing high UV-absorbing components (60% reduction in UV254), accelerated subsequent 55 min H$_2$O$_2$ (50 mmol/L) - UV (25 W) treatment, enhancing its COD & TOC removal efficiency by a factor of 13 & 4, respectively; the combined treatment yielding 25% COD, 50% TOC & complete colour removal (Initial COD = 1476 mg/L; TOC = 336 mg/L).
UV/H$_2$O$_2$/O$_3$	Wastewater containing disperse dyestuff & pigments	99% COD (Initially 930 mg/L) and 96% colour removal in 90 min [pH = 3; H$_2$O$_2$ = 200 mg/L; O$_3$ = 2 g/h; 15 W lamp, 254 nm]. Over 90% removal by UV/O$_3$ with less cost due to no requirement of pH adjustment and H$_2$O$_2$.
Fe^{+2}/O$_3$	Simulated disperse dye bath (CI disperse- violet 931, blue 291; two more azo dyes and compounds)	95% colour (Dyes = 0.5 g/L), 48% COD (initially = 3784 mg/L) removal and 10 times improvement in BOD$_5$/COD ratio at natural acidic pH of dye bath (3.6 mM Fe^{+2}; [Fe^{+2}]: [O$_3$] = 1:14; FeSO$_4$.7H$_2$O = 1000 mg/L). Negligible TOC removal is due to low O$_3$ dose of 14 g/L.
UV/Fenton	DisperseN=N red 354	85% colour removal (dye = 100 mg/L) & 90% COD removal within 10 min with 24.5 mmol H$_2$O$_2$/L and 1.225 mmol FeSO$_4$/L at pH = 3, resulting effluent having only 7.29% inhibition in bioluminescence test. Presence of dispersing agent reduces removal efficiency.
UV/Fenton	Reactive N=N brilliant red X-3B	Stable decolouration (Dye = 7.7×10^{-5} M) within 20 min with [H$_2$O$_2$] = 18 x 10^{-4}M, [Fe+2] or [Fe^{+3}] = 1.1 $\times$ 10^{-4}M, 75 W UV (λ < 32 0 nm) lamp. Use of Fe^{+2} is preferable to Fe^{+3}because of faster reaction rate with H$_2$O$_2$ and evolution of HO instead of HO$_2$.
Solar/Fenton	Orange II (AcidN=N orange 7)	Decolouration of highly concentrated (2.9 mM $\equiv$ 0. 8 g/L) dye in less than 2 h and 95% mineralization within 8 h by a solar simulator (90 mW cm^{-2}) and also by natural sunlight (80 mW cm^{-2}) with 0.92 mM Fe^{+3} and 10 mM H2O2/hr [pH = 2].

Note. Different dye chromophores: N=N: Azo, AQ:Anthraquinone, TPM: Triphenylmethane dye, TH: Thiazine; XN: Xanthene; C=C:Stilbene dye; TC: Phthalocyanine

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Table 5.- List of typical examples of combinations among AOPs for dye wastewater treatment (Adapted from Hai et al., 2007) (continuation)

Technology	Dye/wastewater	Details
Solar/Fenton	MonoreactiveN=N Procion red H-E7B, Hetero-bireactiveN=NRed cibacron FN-R, Standard trichromatic mixture	Sunlight, supplying higher number of photons (3–4 x 10^{-3}W cm^{-2}) than the low power artificial source (350 nm, 6 W, 1.3 x 10^{-4}W cm^{-2}), resulted in faster complete decolouration (15–30 min) and complete (or near) TOC removal (20–60 min) for dye concentration of 100 mg/L with 10 mg/L Fe^{+2} and 100–250 mg/L H_2O_2 [pH = 3].
Cu(II)/gluaric acid/H_2O_2	Direct Chicago sky blueN=N, Methyl orange N=N, Reactive N=N black 5; PolyAQ B-411, ReactiveAQ blue 2, RBBRAQ, Acridin (Basic)AQ orange; Azure blueTH, Crystal violetTPM	Over 90% decolourization of 100 ppm dye within 24 h (70–80% within first 6 h) with 10 mM $CuSO_4$, 200 mM H_2O_2 and low dose of glucaric acid (15 mM). Insensitive to pH, unlike Fenton reaction.
UV/O_3/TiO$_2$	Textile effluent containing ReactiveN=N dye	Removals (60 min)-Photocatalysis (0.1 g/L anatase TiO_2, 125 W, fluency rate 31.1 J m^2 s^{-1}, pH = 11): Colour = 90%, TOC = 50%; Ozonation (pH = 11, 14 mg/L): Colour = 60%, TOC = negligible; Combined: Colour = 100%, TOC > 60%, Toxicity = 50%
UV/H_2O_2/TiO$_2$	Eosin YXN	Enhanced decolouration (100% for 50 mg/L dye) & mineralization (95%) in 1 h (19 W lamp, 1g/L TiO_2, 100 mg/L H2O2, pH = 5.4) along with 85% reduction in toxicity.
Solar/H_2O_2/polymeric metalloporphyrins	Acridin (Basic)AQ orange	% [Decolouration, Degradation]: Hg lamp (450 W, 8 h) Catalysis (3 mg/35 ml) with H_2O_2 (0.4 g/L) = [87, 92]; without H_2O_2 = [77, 86]. Solar light (3 h) Catalysis without H_2O_2 = [77, 90]. Dye = 13.3 mg/L, high pH favourable.
Pulsed streamer corona discharge (electrical)/H_2O_2	Rhodamine B XN (Basic), AcidN=NMethyl orange, DirectN=N Chicago sky blue	Pulsed high voltage (20 kV, 25 Hz) electrical discharge in water, yielding photodissociation of added H_2O_2 (8.8×10^{-4} mol/L), showed enhanced decolouration rate (100% for 10 mg/L dye in 60 min) as compared to individual process- performances.
Photoelectrochemical	Methylene blueTH	Chemical synergism of photochemical & electrochemical processes yielded enhanced decoloration (95%), COD removal (87%) & TOC removal (81%) in 30 min [Dye = 1 mmol/L; 500 W lamp, 6.64 mW cm^{-2}; 1 g TiO_2/200 ml; 30 V DC; Natural pH (6.6)].
Microwave (MW)/Photocatalysis	Rhodamine B XN (Basic)	In contrast to negligible removal by MW (300 W), or less removal by photocatalysis (75W, 0.3 mW cm^{-2}; 30 mg TiO_2/30 ml) alone, combined process achieved 97% decoloration (Dye = 0.05 mM) and 73% TOC removal within 3-h at pH = 5.5.
Photoelectrocatalysis	ReactiveN=N brilliant orange K-R	Decolouration and TOC removal of dye (0.5 mM) in 0.5 mmol l^{-1} NaCl solution within 60 min (Natural pH): i) Adsorption on packed material: 9%, – ; ii) Photocatalysis [TiO_2 (antase = 70%)-coated quartz sand, 500 W high-pressure mercury lamp]: 70%, 20%; iii) Electro-oxidation [30.0 V DC cell voltage, reaction flow rate = 190 ml min^{-1}, 0.05 MPa airflow]: 77%, 7%; iv) Photo-electrocatalysis: 96%, 38%. Obvious enhancement effect (unlike photocatalysis) of salt in solution.
UV/electro-Fenton	ReactiveN=N Red 120	TOC removal [180 min]: 30%; Decolouration [30 min]: 75–85% for 60-100 mg/L concentration; Low efficiency due to radical scavenging by the graphite cathode. Detoxification [90 min]: Safely disposable.
Gamma irradiation/H_2O_2	ReactiveTC blue 15 (Chrozol turquoise blue G), ReactiveN=N black 5 (Chrozol black 5)	H2O2, yielding .OH by reacting with hydrated electron formed in radiolysis of water, achieved enhanced decolouration (100%, 50 ppm dye) and COD removal (76–80%) with 1 and 15 kGy doses for RB5 and RB15, respectively, decolouration (%) being the highest at the lowest dose rate (0.14 kGy/h).

Note. Different dye chromophores: N=N: Azo, AQ:Anthraquinone, TPM: Triphenylmethane dye, TH: Thiazine; XN: Xanthene; C=C:Stilbene dye; TC: Phthalocyanine.

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Table 6.- List of typical examples of combinations among AOPs for dye wastewater treatment (Adapted from Hai et al., 2007) (continuation II)

Technology	Dye/wastewater	Details
Sonolysis/MnO_2	AcidN=N red B	Sonication (50 kHz, 150 W) enhanced oxidation property of MnO_2 (1 g/L) by improving mass transfer, removal of passivating outer oxide layer & production of H2O2, eventually realizing 94.93% decolourization (argon atmosphere) and 48.12 % TOC removal (oxygen atmosphere) [initial pH = 3, 240 min].
Sonolysis /Fenton reaction	AcidN=N Methyl orange	Addition of $FeSO_4$ ([Fe^{+2}] = 0.1–0.5 mM) resulted in Fenton's reaction with H_2O_2 evolving from simultaneous sonification (500 kHz, 50 W) and achieved 3-fold increase in decolouration (15 min, 10 μM dye) and TOC removal (50%, 20 min) as compared to sonification only.
Sonolysis/O_3	C.I ReactiveN=N black 5 (RBB)	Combined sonolysis (520 kHz) and ozonation (irradiation intensity, O_3 input and volume were 1.63 W cm^{-2}; 50 L h^{-1}; and 600 ml) showed synergistic effect, doubling the decolourization (100%, 15 min) and mineralization (76%, 1 h) rate.
Sonolysis/O_3	AcidN=N Methyl orange	Combined sonolysis (500 kHz, 50 W) and ozonation (50V) showed synergistic effect (dead end byproducts of one process being degraded by the other) yielding instant decoloration (10 μM dye) and 80% mineralization (3 h) as compared to 20-30% by stand-alone application.
Sonolysis/UV/O_3	C.I AcidN=N orange 7	Enhanced O_3 (40 g/m^3) diffusion by mechanical effects of ultrasound (520 kHz, 600 W) & the photolysis (108 W) of ultrasound-generated H_2O_2 to produce. OH led to complete decoloration (Dye = 57 μM), 40% TOC removal & an improvement of BOD$_5$/TOC from zero to 0.45 within 60 min (initial pH = 5.5).
Sonolysis /H_2O_2	Vinylsulfone reactive dyes [C.I Reactive- Yellow 15N=N, Red 22N=N, Blue 28, Blue 220, Black 5N=N; Remazol dark black N 150%]	Combined sonolysis (20 kHz) and H_2O_2 (3.49 mol/L) showed synergistic effect, doubling the decolourization (90–99% depending on dye, 4 h) rate.
Sonolysis/UV/H_2O_2	Cuprophenyle yellow RLC=C	Sonication (320 kHz) dramatically enhanced oxidation efficiency of UV(6 at 11 W) + H_2O_2 (0.1 ml/L) system (pH = 11) by improving oxygen uptake & transfer, the combined process achieving 94% dye (0.1 g/L) removal in 60 min following pseudo first-order kinetics.
Sonolysis /UV/TiO_2	Naphthol blue backN=N	Simultaneous or sequential sonolysis (640 kHz, 240 W) and photocatalysis (1g/L TiO_2) showed additive effect on decolouration (100% in 200 min; 50 μM dye) while, in terms of mineralization, simultaneous application (50%, 4 h; 80%, 12 h), due to mass transfer improvement of reactants & products to and from TiO2 surface, performed better than sequential application (<20%, h; 50%, 1 h).
Sonolysis/UV/TiO_2	AcidN=N - red 1, Orange 8	Simultaneous sonolysis (20 kHz, 15 W) and photocatalysis (0.1g/L TiO_2) showed synergistic effect on decolouration/degradation (2.5 $\times$ 10^{-5} M dye) due to promoting de-aggregation of TiO_2, desorption of reactants & products from TiO_2 surface & mainly by scission of produced H_2O_2, thereby, increasing oxidizing species in aqueous phase.
Sonolysis UV/H_2O_2	C.I reactiveN=N red 120	Sonification (320 kHz) significantly enhanced the decolouration (Dye = 0.1 g/L) efficiency of UV/H_2O_2. Higher flow rate (insufficient irradiation) necessitated higher dosing rate of H_2O_2.
Sonoelectrolysis	AcidN=N sandolan Yellow	Electro-oxidation of dye (50 mg/L) in saline solution (0.01 mol/L NaCl) involving in situ generation of hypochlorite ion was enhanced using ultrasound (20 kHz, 22 W) when carried out in a semisealed cell, which minimized the effects of ultrasonic degassing.

Note. Different dye chromophores: N=N: Azo, AQ:Anthraquinone, TPM: Triphenylmethane dye, TH: Thiazine; XN: Xanthene; C=C:Stilbene dye; TC: Phthalocyanine.

Photochemical/Electrochemical

In electrochemical treatments, oxidation is achieved by means of electrodes where a determined difference of potential is applied. On this principle, several different processes have been developed as cathodic and anodic processes: direct and indirect electrochemical oxidation, electrocoagulation, electrodialysis, electromembrane processes, and electrochemical ion exchange. Occasionally, combination of electrochemical technology and photocatalysis has been adopted to yield some unique advantages. For instance, chemical synergism of photocatalysis and electrochemical processes may yield enhanced decoloration and chemical oxygen demand (COD) removal, and added advantage may be derived from existence of salt in solution, which originally is detrimental for sole photocatalysis. Conversely, the electro-Fenton process requires no addition of chemical other than a catalytic quantity of Fe^{+2}, since H_2O_2 is produced in situ, thereby avoiding transport of this hazardous oxidant. In the pulsed high-voltage electric discharge process, addition of oxidants such as H_2O_2 yields highly reactive free radical species through photodissociation of H_2O_2 and thereby enhances the whole process.

Sonolysis and other AOPs

Acoustic cavitation due to ultrasound vibration within a liquid generates local sites of high temperature and pressure for a short period of time, which gives rise to H_2O sonolysis with production of radical species and direct or indirect (via free radicals) destruction of solute. However, stand-alone application of sonolysis hardly results in complete mineralization of pollutant streams containing complex mixtures of organic and inorganic compounds. In view of the substantial amount of energy employed in generating free radicals via acoustic cavitation bubbles, efforts have been made to improve its efficiency. It has frequently been explored in association with other AOPs. For example, combined use of sono-photochemical process can prevent severe mass transfer limitation and reduced efficiency of photocatalyst owing to adsorption of contaminants at the surface. On the other hand, such combination can alleviate the limitations of separate application of sonolysis. A similar advantage has been reported in case of concurrent sonolysis and MnO_2 oxidation. Sonification has also been reported to bring about dramatic enhancement in oxidation efficiency of UV/H_2O_2 by improving oxygen uptake and transfer. Combined application of sonolysis and O_3/UV facilitates O_3 diffusion and photolysis of ultrasound-generated H_2O_2. Such a combination hence yields large number of free radicals. Addition of $FeSO_4$ in solution may result in Fenton reaction with H_2O_2 evolved from simultaneous sonification and may achieve improved decolouration and TOC removal as compared to sonification only. Simultaneous sonolysis has also been reported to enhance electro-oxidation of dye.

3.- AOPs AND OTHER PHYSICOCHEMICAL PROCESSES

Many studies have focused on different combinations among physicochemical systems for treatment of textile and dye wastewaters. Combinations of conventional physicochemical techniques with the AOPs have as well appeared as an attractive option. Tables 7-9 encapsulates information derived from broad spectrum of typical studies dealing with such combinations.

Coagulation-Based Combinations

Coagulation/flocculation/precipitation processes have been used intensively for decolorizing wastewater. For the pretreatment of raw wastewater before discharging to publicly owned treatment plants, these processes may be satisfactory with respect to COD reduction and partial decolourization. Their stand-alone application in treating textile/dye waste is, however, relatively ineffective; for example, only 50% removal was achieved using either alum or ferrous sulphate for an azo reactive yellow dye. In the coagulation process, it is difficult to remove highly water-soluble dyes, and, even more important, the process produces a large quantity of sludge. Nevertheless, researchers are persistent in their pursuit of minimizing the limitations of this technology. For instance, polyaluminum ferric chloride (PAFC), a new type of composite coagulant, was reported to have the advantages of high stability and good coagulating effect for hydrophobic as well as hydrophilic dyes. Its decolouration capacity surpassed that of polyaluminum chloride and polyferric sulfate. On the other hand, to avoid massive sludge disposal problem, different novel approaches, such as coagulation of low-volume segregated dye bath (rather than that of a colossal amount of mixed wastewater), alum sludge recycling, coagulant recovery from textile chemical sludge, reuse of textile sludge in building materials, and processes like vermicomposting of textile mill sludge and coagulation followed by activated carbon adsorption have been proposed. Coagulation followed by adsorption was reported to produce effluent of reuse standard, apart from cutting down the coagulant consumption by 50%, hence lowering the volume of sludge formed, in comparison to coagulation only. Coagulation in combination with advanced oxidation processes, either in sequential or in concurrent manner, has been reported for dye wastewater. For example, simultaneous application of coagulation and Fenton oxidation has revealed improved performance over their stand-alone applications. One of the limitations of the Fenton oxidation process is that large amounts of small, hard-to-settle flocs are consistently observed during the process. Chemical coagulation following Fenton treatment has been found to reduce floc settling time, enhance decolouration, and reduce soluble iron in effluent. Conversely, the photo-Fenton process subsequent to coagulation was reported to complete decolouration and

yield better COD removal, with the added advantage of reducing load on the advanced oxidation process, thereby reducing chemical usage. Investigation on sequential use of coagulation and ozonation revealed the superiority of the scheme involving ozonation preceded by coagulation over the reversed scheme. Multistage application of coagulation followed by ozonation was proved to be superior to their single-pass sequential application (total ozonation time the same). The advantage of the multistage application was more convincing in the case of wastewater with more recalcitrant composition.
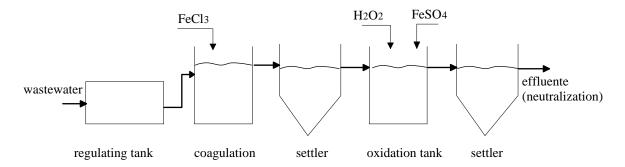

Figure 5.- Scheme of physicochemical process combined with Fenton process for textile dyeing wastewater treatment

Adsorption-Based Combinations

Adsorption techniques, specially the excellent adsorption properties of carbon-based supports, have been utilized for the decolourization of dyes in the industrial effluents. Activated carbon, either in powder or granular form, is the most widely used adsorbent for this purpose because of its extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. It is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent dispersed, direct, vat, pigment, and reactive dyes. However, the use of carbon adsorption for decolourization of raw wastewater is impractical because of competition between coloured molecules and other organic/inorganic compounds. Hence, its use has been recommended as a polishing step or as an emergency unit at the end of treatment stage to meet the discharge colour standards. The fact that activated carbon is expensive and weight loss is inevitable during its costly on-site regeneration (10% loss in the thermal regeneration process) impedes its widespread use. Utilization of nonconventional, economical sources (industrial or agricultural by-products) rather than usual relatively expensive materials (coconut shell, wood or coal) as precursors for activated carbon has been proposed to achieve cost-effectiveness in its application. There has been considerable interest in using low-cost adsorbents for decolourization of wastewater. These materials include chitosan, zeolite, and clay; certain waste products from industrial operations such as fly ash, coal, and oxides; agricultural wastes and lignocellusic wastes; and so on. Each of the non-regenerable economical adsorbents has its specific drawbacks and advantages; all, however, pose further disposal problem. To do away with the disposal problem, easily regenerable adsorbent is required. As mentioned earlier, adsorption is a nondestructive method involving only phase change of pollutants, and hence imposes further problem in the form of sludge disposal. The high cost of adsorbent also necessitates its regeneration.

Conversely, some catalytic oxidation/reduction systems appear to be more efficient when treating small volumes of concentrated dyes. So it appears attractive to combine adsorption with some other process in a system where contaminants are preconcentrated on adsorbent and then separated from water. The contaminants thus separated may subsequently be mineralized, for example, by wet air oxidation, or degraded to some extent, for instance, with azo bond reduction by bisulfite-mediated borohydride so as to regenerate the adsorbent and reuse. In this way an economical process coupling two treatment technologies eliminating their inherent drawbacks may be developed. If partial degradation is applied to regenerate the adsorbent, it will still leave behind a small volume of wastewater (as compared to the volume that existed before adsorption) to be treated. This again can be conveniently taken care of by applying some AOP. Ince and Apikyan (2000) proposed a slightly modified version of the aforementioned so-called "phase-transfer oxidation." Their strategy was comprised of simultaneous operation of adsorption and AOP followed by periodic on-site destructive regeneration of the spent adsorbent. Adsorption concurrent with ozonation, UV–H_2O_2, or microwave-induced oxidation has been reported to yield mutual enhancements like catalysis of AOP by adsorbent and simultaneous regeneration of adsorbent. A rather elaborate method involving solvent extraction and catalytic oxidation has been documented in the literature. The method consists of dye extraction using an economical solvent followed by dye recovery through chemical stripping. In this way the solvent is also regenerated. Finally, treatment of the extraction raffinate can be achieved by catalytic oxidation.

Membrane-Based Combinations

Membrane separation endows the options of either concentrating the dyestuffs and auxiliaries and producing purified water, or removing the dyestuff and allowing reuse of water along with auxiliary chemicals, or even realizing recovery of considerable portion of dye, auxiliaries, and water altogether. Such recovery/reuse practice reduces many-fold the recurring cost for the treatment of waste streams. The fact that the dyeing behaviour of the residual dye should ideally be identical to that of the fresh dye may restrict dye recovery and reuse to specific dye classes. Accordingly, water and/or electrolyte recovery from dye bath effluent has become the focus of the contemporary literature. However, concentrated sludge production and occurrence of frequent membrane fouling requiring costly membrane replacement impede widespread use of this technology. Two distinct trends are hence notable among the reported studies that couple membrane separation with other technologies. Some studies mainly focus on alleviation of the membrane-concentrate disposal problem, while others seek to offer complete hybrid systems wherein elimination of the limitations of the membrane technology (e.g., fouling) and/or those of the counterpart technologies (e.g., ultrafine catalyst separation in photocatalysis) may be expected.

Hybrid processes based on membrane and photocatalysis have been reported to eradicate the problem of ultrafine catalyst to be separated from the treated liquid in case of slurry reactors, with the added advantage of membrane acting as selective barrier for the species to be degraded. On the other hand, in case of immobilized catalysis, membrane may play the role of support for the photocatalyst. For coupling with photocatalysis, membrane distillation, however, has been reported to be more beneficial in comparison with pressure-driven membrane process, as significant fouling may be associated with the latter. Tay et al. (2001) proposed a photo-oxidative ($UV/TiO_2/H_2O_2$) pretreatment prior to membrane filtration to partially break down the high-molecular-weight compounds that cause membrane fouling.

The relatively smaller fragments produced therefrom were still retainable by membrane, and, unlike the parent compounds, they did not affect the charge of the membrane surface. Membrane contactors, involving mass transfer in the pores by diffusion (avoiding gas dispersion as macroscopic bubbles as in traditional ozonation systems), offer the advantages of higher contact surface (equal to membrane surface, which may reach up to 30 km^2/m^3 H_2O for hollow-fibre membranes), easy scale-up, no foam formation, and lower process cost (no requirement of ozone destruction, lower ozone loss). Numerous studies have reported on application of membrane filtration (ultrafiltration/nanofiltration, UF/NF) following coagulation/flocculation to produce reusable water. Such application has the added advantage of minimizing membrane fouling. In this context, the hybrid coagulation membrane reactor may offer another viable option. This treatment scheme may also be placed subsequent to advanced oxidation processes in order to remove soluble degradation products.

Application of separate technologies for segregated streams has been recommended by different researchers. For instance, Wenzel et al. (1996) recommended hot water reuse in rinsing after reclamation by membrane, and reuse of dye bath water and salts after adsorption of dyestuff and COD on activated carbon. Conversely, the hybrid adsorption-membrane reactor, offering synergism in that the compounds too large to be adsorbed onto adsorbent are successfully retained by the membrane while low-molecular-weight organics are well adsorbed on adsorbent, is also worth mentioning.

A considerable number of studies have been devoted to eradication of the major drawback associated with membrane separation, that is, concentrated residue remaining for disposal. As mentioned earlier, dyes in the concentrate from the membrane separation unit, because of the usual quality requirements for the colour shades in the dyed products, cannot be reused and must be treated before discharge. In this respect, catalyzed wet air oxidation (WAO) has emerged as an efficient system. Sonification was found essential to make the membrane retentate from actual wastewater be amenable to subsequent WAO. On the other hand, augmentation of advanced oxidation process (e.g., ozonation) subsequent to membrane filtration has been envisaged as a scheme yielding several advantages, such as reducing waste volume for oxidation while simultaneously recovering salt, and, in addition, limiting concentrated waste for disposal. A novel membrane-based integrated water management system for the exhausted dye bath and rinsing bath was proposed by Bruggen et al. (2004). The proposed scheme involved, in order of application, microfiltration membrane (pretreatment), loose nanofiltration membrane (NF-1, for organics removal), and another tighter NF membrane (NF-2, salt retention). According to that scheme, further separation of organic fraction may be achieved by membrane distillation units, while retained salt may be recovered through membrane crystallization. Finally, the organic sludge of high calorific value from the membrane distillation unit may be incinerated.

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Table 7 .- Typical Examples of Combinations Between Conventional Physicochemical Processes and AOPs (Adapted from Hai et al., 2007)

Technology	Dye/wastewater	Details
Fenton/chemical coagulation	C.I directN=N blue 202, C.I reactiveN=N black 5; PVA	81–86% COD (Initially > 1000 mg/L) removal & decolouration (Dye=200 mg/L) in 2 h with [H_2O_2]/[$FeSO_4$] = 1000/400 at pH=3, while subsequent coagulation at pH=7–10 with 100 mg/L PAC & 2 mg/L polymer reduced floc settling time, enhanced decolouration and reduced soluble Fe in effluent.
Fenton+ chemical coagulation	Disperse-BlueN=N 106, YellowAQ 54; Reactive- BlueAQ 49, YellowN=N 84	Coagulation (pH = 5–7): Removal per mol Fe^{+3}[COD, DYE]: Disperse (0.74–0.93 mM $FeCl_3$) = [460.2–477g, 525.7–672.7]; Reactive (1.85–2.78 mM $FeCl_3$) = [37.4–86.5 g, 109.5–192.7 g]. Fenton (pH=3; 30 min; [Fe^{+2}]: [H_2O_2] = 1:0.2–1:0.37): Removal per mol Fe^{+2} [COD, DYE]: Disperse = [14–80g, 3.7–20.8g]; Reactive = [114.2–199.6g, 118.9–489.2g]. Combined: Both dyes, 90% COD & 99% dye removal.
O_3/coagulation	Azo dye manufacturing wastewater (subjected to chlorination)	Removal: After Ozonation [70 min; 56 mg O_3/min; 1.6 L/min; pH=10.3] COD = 25%, Colour = 43%. After subsequent Ca (OH)$_2$ coagulation [787 mg/L, pH = 12] COD = 50%, TOC = 42%, Color = 62%.; effective removal of chloro-organics after two stages.
Coagulation/O_3	Textile wastewater	Coagulation [$Al_2(SO_4)_3$, 60 ppm; polyelectrolyte 0.6 ppm] resulted in 65–75% & 20% reduction of COD & absorbance (initial COD = 890 mg/L), while subsequent ozonation (3 mg/min, 10–15 min) gave a further 90% & 20–25% reduction of residual color & COD. Ozonation preceded by coagulation gave worse result.
Multistage (coagulation/O_3)	Dye manufacturing wastewater	Single stage coagulation (2.5%, v/v, $FeCl_2$; 35 mg/L polymer; pH = 8.5) followed by ozonation (pH = 11; 90 min) achieved [19% COD, 88% colour] and [67% COD, 99.3% colour] removal, respectively (initial COD = 7700 mg/L; Colour = 67000 ADMI). Three times repetition of the sequence while keeping total ozonation time same (3 at 30 min) achieved >90% COD & 99.99% colour removal, the superiority of multistage treatment being less convincing for wastewater with simpler composition.
Coagulation/UV Fenton	Integrated plant containing variety of processes ranging from desizing to dyeing and ultimate finishing	UV (20 W)/TiO_2 (1 g/L)/H_2O_2(10 mM)/Fe^{+2}(1 mM) treatment (pH=4) following coagulation treatment achieved complete decolouration (30 min) & a maximal 48% (over that achieved by coagulation) COD removal (1 h), the COD of raw, coagulated, and oxidized sample being 1063, 556, & 269 mg/L, respectively.
Coagulation/ carbon adsorption	C.I reactiveN=N red 45, C.I reactiveN=N green 8	Removal (Dye = 1g/L): After $AlCl_3 \cdot 6H_2O$ coagulation [0.8 g/L; pH = 3.5]: RR 45 [Colour 98.8%, TOC 98.1%, COD 93.4%]; RG 8 [Colour 99%, TOC 96.9%, COD 83.8%]. After carbon adsorption [0.24 & 0.84 g/L; 2 hr]: RR 45 [Colour 99.9%, TOC 99.7%, COD 95.7%]; RG 8[Colour 99.9%, TOC 99.2%, COD 91.3%]. Half the coagulant consumption and lower volume of sludge formation in comparison to dye removal by coagulation only.
Photocatalysis/ adsorption (powdered activated carbon, PAC)	Humic acid (natural coloring matter)	3–4 h irradiation induced decrease in UV280, UV254, TOC and COD and simultaneous improvement of biodegradability with no significant decrease in adsorptivity of subsequent PAC.
Adsorption (fluidized GAC) +O_3	Acid blue 9, MordantN=N black 11, ReactiveAQ blue 19, ReactiveN=N orange 16	Influent: pH = 5.1–9.2, COD = 250–1800 mg/1, SS = 45–320 mg/, turbidity (NTU) = 50 –210. Combined ozonation and GAC adsorption (4 L O_3/min per 100 gm GAC) offers mutual enhancement namely regeneration of GAC & catalysis of O_3.

Note. Different dye chromophores: N=N:Azo, AQ: Anthraquinone, TC: Phthalocyanine.

Table 8.- Typical Examples of Combinations Between Conventional Physicochemical Processes and AOPs (Adapted from Hai et al., 2007) (continuation)

Technology	Dye/wastewater	Details
Adsorption (GAC) +UV/H$_2$O$_2$	Reactive Everzol Black–GSP	Simultaneous adsorption (8 g/L) & UV– H$_2$O$_2$ oxidation (0.009 M) achieved synergistic decoloration & TOC removal (complete & 50%, 30min) for the originally poorly adsorbable dye (36 ppm) concurrent with cost saving due to reuse of adsorbent.
Adsorption (β-FeOOH)/ oxidative (H$_2$O$_2$) regeneration	C.I. ReactiveN=N Red 198	Adsorption onto granulated β-FeOOH (170 mg/g) and its repeated reuse (6 cycles) following regeneration by catalytic oxidation using H$_2$O$_2$ (7 mg dye/mg; 6 h at 24.5 ml/min); selective adsorption/oxidation, lower oxidant dose and no conventional concentrate treatment. Simultaneous treatment recommended for high salt-containing wastewater.
Adsorption (PAC)/wet air oxidation (WAO)	Chemictive Brill. Blue R (ReactiveAQ); Cibacorn Turquoise Blue G (ReactiveTC)	Efficient treatment of lower concentrations of unhydrolized reactive dyes by first adsorbing on PAC, and subsequently, regenerating (>98% after consecutive 4 cycles with only 8% total weight loss) spent PAC by WAO (150–250∘C, O$_2$ partial pressure 0.69–1.38 Mpa), and recycling the regenerated carbon.
Ion-exchanger (quarternized ammonium cellulose) /chemical reduction (bisulfite-mediated borohydride)	Orange II (AcidN=N Orange 7), ReactiveN=N red 180	Anion exchanger bound 383 mg/g of Orange II & 272 mg/g of reactive dye while subsequent KBH$_4$/NaHSO$_3$ (2 mM/10 mM) reduction of dye (1 mM solution) followed by salt or base extraction resulted in almost complete regeneration of the costly ion exchanger, establishing a feasible process coupling two technologies with limited potential alone.
Adsorption (CuFe$_2$O$_4$)/ catalytic combustion	AcidN=N Red B	Dye, preconcentrated on adsorbent/catalyst CuFe$_2$O$_4$ (>95% removal from 100 mg/L; pH <5.5, dose = 0.1 g/50 ml), after magnetic solid/liquid separation, was subject to complete combustion at relatively low temp (300∘C) without evolution of harmful products; and in the process, CuFe$_2$O$_4$ was regenerated allowing efficient reuse over extended cycles.
Adsorption (ferrous modified GAC) + microwave (MW) induced Oxidation	Argazol Blue BF-BR 150% (bifunctionalN=N reactive dye)	98.3% decoloration and 96.8% COD removal was achieved when dye solution (50 ml, 300 mg/L) containing ferrous modified GAC (2 g) was subject to MW irradiation (5 min, 500W, 2450 MHz), the removal mechanism involving GAC adsorption & subsequent combustion (induced by MW) on its surface. Negligible stripping of Fe^{+2} from GAC surface under reuse for many times.
Adsorption (GAC)/microwave (MW) regeneration	C.I AcidN=N Orange 7	Dye (500 mg/L)- exhausted GAC could be successfully regenerated by microwave irradiation (2450 MHz, 850 W, 5 min) for repeated cycles involving low GAC loss (6.5%, 4 cycles) and adsorption rate even higher than that of virgin GAC due to pore-size distribution & surface chemistry modification.
Sonication/FeO reduction	C.I AcidN=N Orange 7	Pulsed sonication (20 kHz, 250 W), by improving mass transfer & also increasing active sites on Fe-surface, dramatically enhanced dye (50 mg/L) decoloration efficiency of mild reducing agent Fe0 (1 g/L, pH=3), the combined process achieving 91% dye removal in 30 min following 1st order kinetics.
Membrane based ozonator	Blue 19 reactive dye; Untreated exhausted dye-bath	Thin coating of TiO$_2$ & γ-Al$_2$O$_3$ on ceramic membrane (ZrO$_2$, α-Al$_2$O$_3$) eliminated defects & hence allowed operation at high gas pressure with substantial ozone transfer improvement, eventually yielding 100% & 62% decoloration of pure dye (0.072 mmol/L) & untreated dye bath, respectively, in 2 h

Note. Different dye chromophores: N=N:Azo, AQ: Anthraquinone, TC: Phthalocyanine.

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Table 9.- Typical Examples of Combinations Between Conventional Physicochemical Processes and AOPs (Adapted from Hai et al., 2007) (continuation II)

Technology	Dye/wastewater	Details
Membrane/wet air oxidation, WAO	DisperseN=N blue CI 79	NF membrane achieved >99% colour and 97% COD rejection of dye compound while the homogeneous copper sulfate catalyzed WAO (160°–225°C, O_2 partial pressure 0.69–1.38 Mpa) reduced 90% COD from concentrate (120 min).
Membrane/wet air oxidation, WAO	Dyeing wastewater containing Reactive blue, Indigo, Sulfur black & other process chemicals	Replacing O_2 with stronger oxidant H_2O_2 (50% of stoichiometric amount) & adding Cu-AC catalyst (2 g/L), 80% TOC & 90% colour was removed from membrane concentrate by WO under mild condition (110°C ,Total P = 50 kPa) in 30 min
Membrane/sonic ation/ WAO	ReactiveTC Turquoise blue CI25	NF membrane (1.5 Mpa; flux = 0.084 m/h) removed 90.3% COD & 98.7% color from *pure dye solution* (COD = 1500 mg/L), while WO (190°C, O_2 pressure = 0.69 Mpa; pH = 7) reduced 90% COD from diluted (COD = 500–700 mg/L) concentrate (120 min). Sonication (150/350 W, avg./peak; 40 kHz; 30 min) was essential to make membrane retentate from *actual wastewater* to be amenable to subsequent WO.
Membrane/O_3	Reactive (Remazol blue BB , Intracorn golden yellow VS-GA, Remazol red RB) & salt	NF membrane (9.41L/min; Re = 838) generated reusable permeate (85% of original volume) with >99% of colour & Cu, and only 15% of salt removal while subsequent ozonation (7.73 mg/L.min, pH = 11) removed colour from the concentrate following 1st order kinetics, the rate decreasing with increasing initial dye colour.
UV-Fenton/coagulation /membrane	ReactiveN=N (Procion Red HE7B)	Complete color removal (Dye = 50 mg/L) and 79% TOC removal within 20 min by photo-Fenton (pH = 3; $[H_2O_2]/[Fe^{+2}]$ = 20:1; 4 at 15 W UV lamp). However 9 times increase in dissolved solids warrants subsequent coagulation/membrane system for reuse in dye/rinse process.
Physicochemical/ membrane (UF/NF)	Synthetic textile manufacturing wastewater	Raw water: Conductivity (mS/cm) 2.06; S.S. (mg/L) 82.6; COD (mg/L) 1640; Turbidity (NTU) 15.65; In order to reuse the water in rinse processes, it is necessary a negligible COD and a conductivity lower than 1 mS/cm. Physicochemical (pH = 8.5, CDK–FER20 = 200 mg/L, Cnalco,flocculant = 1 mg/L): 50% COD removal; NF membrane (flow rate = 400 L/h, TMP = 1 MPa): 100% COD removal, 85% conductivity retention.[Reusable]
Physicochemical/ membrane (NF)	Textile wastewater	Raw water: Conductivity (mS/cm) 4.53; COD (mg/L) 1630. Physicochemical (pH=12, Fe^{+2}=700 mg/L): 72.5% COD removal; NF membrane (flow rate = 200 L/h, TMP = 20 bar, flux = 8–10 L/m²h): COD<100 mg/L; Conductivity <1 mS/cm
Clariflocculation/ ozonation/ membrane (UF)	Wastewater from carbonizing process, from dyeing and fulling	49% turbidity & 71% color removal by clariflocculation & ozonation, respectively, and high turbidity (27%) & TSS (30%) removal by the subsequent UF membrane contributed to achievement of final 66% COD and 93% color removal, making reuse, after 50% dilution with well water, possible.
Activated C/membrane (NF/RO)	Reactive dye for cotton	Hot water reuse in rinsing after reclamation by membrane (degradation of filtration remanence in anaerobic digesters); and reuse of dye bath water and salts after adsorption of dyestuff and COD on activated carbon.
Membrane (UF)/adsorption (activated carbon cloth, ACC)	AcidN=N Orange II, AcidN=N Brilliant Yellow (color) & Bentonite (turbidity)	Both process are complementary in that compounds too large to be adsorbed onto ACC are successfully retained by the membrane (>98% turbidity & 15–40% dye removal), while low-molecular-weight organics are well adsorbed by the ACC (38–180 mg/g, dye-specific). Replacing UF with NF, or UF membrane wrapped up in a pleated ACC recommended to avoid early breakthrough of ACC.

Note. Different dye chromophores: N=N:Azo, AQ: Anthraquinone, TC: Phthalocyanine.

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4. - BIOLOGICAL TREATMENT-BASED COMBINATIONS

4.1.- Combination among biological processes

Conventionally a chemical coagulation step, preceded by or antecedent to biological treatment, is applied for dye wastewater. Combined treatment with municipal wastewaters is usually favoured wherever applicable.

Various biological treatment processes including activated sludge, fluidized biofilm, different fixed film systems, or combinations thereof have been employed. Although in case of aerobic bacteria cometabolic reductive cleavage of azo dyes as well as utilization of azo compounds as sole source of carbon and energy (leading to mineralization) have been reported, dyes are generally very resistant to degradation under aerobic conditions. Toxicity of dye wastewater and factors inhibiting permeation of the dye through the microbial cell membrane reduce the effectiveness of biological degradation.

Dyestuff removal, hence, currently occurs in the primary settling tank of a wastewater treatment plant for the water-insoluble dye classes (disperse, vat, sulphur, azoic dyes), while the main removal mechanism for the water soluble basic and direct dyes in conventional aerobic systems is adsorption to the biological sludge. Reactive and acid dyes, however, adsorb very poorly to sludge and are thus major troublemakers in relation to residual colour in discharged effluents. Since reduction of the azo bond can be achieved under the reducing conditions prevailing in anaerobic bioreactors and the resulting colourless aromatic amines may be mineralized under aerobic conditions, a combined anaerobic-aerobic azo dye treatment system appears to be attractive. Trials with various combinations, including simultaneous anaerobic/aerobic process (microbial immobilization on a matrix providing oxygen gradient or an anaerobic–aerobic hybrid reactor), anoxic plus anaerobic/aerobic process, anaerobic/oxic system, and aerobic (cell growth)/anaerobic (decolourization) system, have all been explored, involving fed batch, sequencing batch, or continuous feeding strategies, with encouraging results. Both cytoplasmic and membrane-bound unspecific azo-reductase activities under anaerobic condition have been reported. Glucose, raw municipal wastewater, and yeast extract, among others, have been reported as examples of an essential co-substrate needed to obtain good anaerobic colour removal.

Different abiotic processes involving derivatives generated during bacterial downloaded by metabolism (e.g., sulphide, amino acid cysteine, ascorbate) may contribute in decolourization under anaerobic conditions. The biotic process, however, dominates in high-rate anaerobic bioreactors. Addition of redox-mediating compounds like anthraquinone sulfonate or anthraquinone disulfonate has been reported to greatly enhance both the biotic and abiotic processes.

However, during post-treatment of anaerobically treated azo dye-containing wastewater, there will be competition between biodegradation and autoxidation of aromatic amines. This may be problematic not only because the formed products are coloured but also because some of these compounds, such as azoxy compounds, may cause toxicity. It should be emphasized that in high-nitrogen waste waters it makes little sense to remove part of COD by anaerobic treatment in the first step when COD has to be added again to the effluent afterward in order to achieve nitrogen removal. Biological treatment is a cost-competitive and eco-friendly alternative.

Researchers are hence persistent in their pursuit of minimizing the inherent limitations of biological dye wastewater treatments. Several innovative attempts to achieve improved reactor design and/or to utilize special dye degrading microbes or to integrate textile production with wastewater treatment have been documented in literature. Some of these innovative endeavours include a two-stage activated sludge process (high-load first stage, achieving biosorption and incipient decomposition of high-molecular-weight organic compounds, followed by a low-load polishing stage); high-rate anaerobic systems uncoupling hydraulic retention time from solids retention time; two-phase anaerobic treatment wherein the acidic-phase bioreactor is also shared for textile production (integration of production with wastewater treatment); activated sludge pre-treatment, to reduce organic nitrogen, before fungi decolouration; fungi pre-treatment before anaerobic treatment; combined fungi (biofilm) and activated sludge culture for decolouration; activated algae reactor (with mixed population of algae and bacteria); activated sludge followed by over land flow; etc.

4.2.- Hybrid Technologies Based on Biological Processes

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 (Vandevivere et al., 1998).

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Figure 6.- Water processes train of Alto Lura WWTP managed by CIDA Srl in the Como area (Italy) and treating 22.000 m³/day 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). (Adapted from Vandevivere et al., 1998).
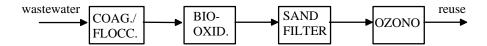

Figure 7.- Water processes train of Levi's Strauss WWTP, Wervik (Belgium). (Adapted from Vandevivere et al., 1998).

Table 10-12 summarize a broad spectrum of intriguing reports on hybrid technologies having biological processes as the core.

Integrated partial oxidation/biodegradation

In contrast to the conventional pre- or post- treatment concepts, where process designs of different components are independent of each other, a rather innovative approach is the so-called "integrated processes" where the effectiveness of combining biological and other treatments is specifically designed to be synergetic rather than additive. A typical example of such processes is combination of advanced oxidation with an activated sludge treatment where the chemical oxidation is specifically aimed to partially degrade the recalcitrant contaminants to more easily biodegradable intermediates, thereby enhancing subsequent biological unit and simultaneously avoiding the high costs of total mineralization by AOP. During recent years myriad studies dealing with partial pre-oxidation of dye wastewater, involving virtually all sorts of AOPs, have been reported. Some of these studies include partial oxidation by ozonation, H_2O_2, photocatalysis, photo (solar)-Fenton, wet air oxidation, combined photocatalysis and ozonation/H_2O_2, photoelectrochemical process, sub- and supercritical water oxidation, and electron-beam treatment. The bulk of such studies report on improvement of biodegradability (as revealed by biological oxygen demand BOD/COD ratio or partial oxidation parameter) and reduction of toxicity (using bioassay, e.g., bioluminescence test) following some AOP treatment without involving actual experiment in biological reactor. However, complete results from actual investigation in biological system following partial oxidation, as listed in Tables 10-12, are also available. Careful consideration of characteristics of each AOP would facilitate selection of a proper preoxidation process for rendering wastewater more amenable to biological treatment. Forinstance, Fenton-like treatment using Nafion-Fe^{+3} membrane, rather than direct addition of iron salt, or immobilized TiO2 photocatalysis rather than the photo-Fenton process, would facilitate further biological treatment under biocompatible pH making neutralization redundant. Mantzavinos and Psillakis (2004) have proposed a step-by-step approach to evaluate chemical pretreatment for integrated systems.

The combined oxidation and subsequent biodegradation make it necessary to set the optimal point of oxidative treatment. Further oxidation may not lead to any significant changes in the molecular weight distribution, but result in an increasing mineralization of low-molecular-weight biodegradable substances. Hence it is rational to adopt the shortest possible peroxidation period and remove the biodegradable portion using cost-effective biological process. Nonetheless, the extent of combined COD removal achievable with this strategy may be limited in some cases, making utilization of a longer oxidation period necessary and the following biological process redundant.

An internal recycle between the oxidation and biological stage has been recommended for reducing chemical dose in such circumstances. Dogruel et al. (2002) pointed to the selective preference of ozone for simpler readily biodegradable soluble COD fractions, which leads to unnecessary consumption of the chemical. They suggested pre-ozonation of segregated recalcitrant streams from the dye house prior to biological treatment of the mixed whole effluent. If a considerable amount of biodegradable compounds originally exists in the wastewater, the pre-oxidation step obviously will not lead to a significant improvement of biodegradability; rather, it will cause unnecessary consumption of chemicals. In such a case a biological pre-treatment (removing biodegradable compounds) followed by an AOP (converting non-biodegradable portion to biodegradable compounds with less chemical consumption) and a biological polishing step may prove to be more useful.

Anaerobic biological treatment has also been combined with photocatalysis with immobilised TiO_2 (as a pre- or post-oxidation method) to treat raw solutions of azo, anthraquinone and phthalocyanine textile dyes (Harrelkas et al., 2008). Muhammad et al. (2008) pointed to the decolorization of biotreated textile dye bath effluent was most efficient, and reached up to 95% in the cases of both ozone and UV/H_2O_2. COD removal in all AOPs was found to occur in the following descending order UV/H_2O_2, UV, O_3 and photoFenton. UV/H_2O_2 was the most efficient in terms of both COD and color removal. It can also be presumed that the simultaneous application of UV and H_2O_2 to biotreated effluent is a promising AOP technique for potential industrial implementation.

Table 10.- List of examples of combinations between biological treatment and other technologies (textile wastewater and mixings) (Adapted from Hai et al., 2007)

Technology	Dye/Wastewater	Details
Polyurethane immobilized fluidized biofilm/ coagulation (alum)	Dyeing wastewater from polyester deweighted process	92% CODMn (initially 824 mg/L) removal by biological (0.16–0.32 kg CODMn/kg VSS.day) followed by coagulation (600 mg/L alum, pH = 6) process. Coagulation (1000 mg/L alum, pH = 6) followed by biological (0.09–0.19 kg CODMn/kg VSS.day) process achieved similar removal, but with 20% more excess sludge due to more dissolved (in addition to suspended) substance removal during coagulation.
Coagulation (Na-bentonite) / Activated sludge	Wastewater from plants dyeing & finishing natural/synthetic fibres	Chemical pre-treatment (2 g/L) prior to biological process reduced 40% of initial biodegradable as well as inert soluble COD, thereby reduced potential of 'residual inert COD (products from biodegradable COD)', while chemical post-treatment following biological, achieved, despite better decolouration, only 20% residual soluble COD removal.
Fluidized biofilm/ coagulation/ electrochemical oxidation	Synthetic textile dyeing wastewater	Biofilm of specially isolated microbes on support media achieved 68.8% CODcr (initial = 800–1000 mg/L) and 54.5% colour removal while those achieved by overall combined system ($FeCl_3.6H_2O$ dose of 3.25×10^{-3} mol/L; Electro-oxidation: 2.1 mA/cm² of current density and 0.7 L/min flow rate) were 95.4% and 98.5%, respectively.
Coagulation/electrochemical oxidation/activated sludge	15 dyes used in a plant making primarily cotton and polyester fibres and small quantity of wool	Influent: COD = 800–1600 mg/L, Transparency <4 cm, Conductivity = 2000 μS/cm, pH = 6–9. COD concentration (100 mg/L) and transparency (30) amply satisfies the government safe discharge standard by employing Poly aluminum chloride (40 mg/L, with polymer concentration 0.5 mg/L), electrochemical oxidation (pH≈7, current density = 53.4 mA/cm², 1 L/min of flow rate) and the subsequent activated sludge process.
Bio/ electroflocculation/ flotation/filtration	Wastewater from plants dyeing & finishing natural/synthetic fibres	Although electro-flocculation is effective without biological pre-treatment, the same enhanced its performance, while subsequent flotation and bentonite filtration completed sludge removal & lowered Fe concentration, the combined system achieving complete colour, 69% COD & appreciable salt removal. Al-electrode should be preferred to Fe-electrode to avoid residual Fe interfering reuse of wastewater for dyeing light colours.
O_3/coagulation/ activated sludge	Textile wastewater	Complete decolourization of the textile effluent (COD = 1800 mg/L, JTU transparency = 2 cm) accomplished with 10 min ozonation (rate 13.25 g/h). Without/With coagulation (3 ml PAC) only 5% and up to 70% COD reduction, respectively.
Coagulation/ activated sludge/overland flow	Cotton textile wastewater	Input COD, TDS and Turbidity (2009 mg/L, 2987 mg/L, 102 NTU) reduced as follows: After Physicochemical [$Alum_{416 mg/L}$, $lime_{213 mg/L}$, $polyelectrolyte_{11 mg/L}$]: (1054 mg/L, 1540 mg/L, 52 NTU); After Activated sludge [HRT = 20 hr, COD loading-0.9 kg COD/m³, MLSS-3073 mg/L, sludge recycle-20%]: (488 mg/L, 772 mg/L, 49 NTU); After land treatment: (89 mg/L, 239 mg/L, 20 NTU).
Coagulation/ activated sludge, AS/filtration/ disinfection	Textile wastewater	[BOD_5 (mg/L), COD (mg/L), Conductivity (μS/cm)]: Influent = [940, 2560, 3500]; After chemical treatment ($FeSO_4. 7H_2O$ = 0.72 kg/m³, Polyelectrolyte = 0.2 g/m³) = [512, 1250, 2940]; After tertiary = [15, 310, 2800], reusable for irrigation.
Bio (*Phanerochaete chrysosporium* fungi)/O_3	Textile wastewater	Decrease in high molecular mass fraction of textile effluent in the biological process (pH = 4.5) & low molecular mass fraction during subsequent O_3 treatment (pH = 11, 15 L/h, 80 min) accompanied by 40% decolouration in each step, the final effluent showing no toxicity.

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Table 11.- List of examples of combinations between biological treatment and other technologies (textile wastewater and mixings) (Adapted from Hai et al., 2007) (continuation)

Technology	Dye/Wastewater	Details
Electron-beam treatment/bio	Mixed raw wastewater predominately from dyeing process & 8% from polyester fibre production	Pilot plant investigation (flow rate = 1000 m^3/d) involving low dose (1 kGy) E-beam pre-treatment revealed enhanced bio treatment performance requiring reduced (half) residence time (HRT) for same degree of removal. With the wastewater being originally biodegradable, the role of E-beam was, in contrast to usual anticipation of conversion of non-biodegradable portion, to convert the biodegradable portion to further easier forms.
Clariflocculation/ bio/ AOP (H_2O_2/UV)	Wool scouring effluent	Clariflocculation followed by aerobic biological treatment removed >90% COD & all BOD; however, remaining COD (1000 mg/L) & intense colour warranted subsequent H_2O_2/UV [Molar ratio, COD:H_2O_2 = 1:1; 40 W] treatment which, despite presence of strong UV absorbing compounds, achieved 100% decolouration (30 min), 75% COD & 85% TOC removal (60 min) irrespective of pH.
Bio/flocculation/ $O_3+H_2O_2$	Textile wastewater	Activated sludge treatment followed by flocculation realized 85%, 99.5% & 85% DOC, BOD & CODcr removal (Initial values, mg/L, 277, 220, 780), while subsequent O_3+ H_2O_2 treatment (60 min; [H_2O_2]:[DOC] = 1:1) achieved complete removal of BOD & over 50% removal of residual DOC, CODcr. Conversely, single ozonation resulted in lower COD removal and increased BOD (biodegradability).
[O_3]/bio/[O_3]	Wastewater from plants dyeing & finishing natural/synthetic fibres	Pre-ozonation, due to selective preference of O_3 for simpler organic compound, significantly decreased readily biodegradable COD without appreciably affecting soluble inert COD. Post-ozonation achieved higher colour and inert COD removal involving 50% less ozone dose compared to pre-ozonation at same contact time & ozone flux rate.
Bio/sand filter (SF)/O_3	Wastewater from plants dyeing & finishing natural/synthetic fibres	Removal of suspended solid (& hence COD) by biological & SF pre-treatment enhanced subsequent two sequences of ozonation (30 min, 40 g/m^3), achieving, in contrast to 60% COD removal by ozonation alone (without pre-treatment), a combined 65% & 78% COD removal after first & second ozonation cycle, respectively. Complete decolouration allowed wastewater reuse in dyeing even light colours.
Biological+ physicochemical/ O_3	Jeans finishing plant wastewater mixed with domestic WW (<30%)	Pre-treatment involving GAC (200 g/L) & polyelectrolyte addition in anaerobic reactor restored nitrification activity & improved sludge settleability of the subsequent aerobic reactor with a cumulative 96% COD & 88% colour removal, while following ozonation achieved 70% reusable water.
Bio/O_3/granular activated C(GAC)	Domestic + textile industry (50–70%) wastewater	Feed water [on GAC]: COD = 128–135 mg/L, TOC = 16–18 mg/L; C-adsorption is less effective after the ozonation, residual COD (>70) & colour (over optical detection) unsuitable for reuse; "Bio+Flocculation+O_3+GAC" proposed.
Bio (anoxic/aerobic)/ oxygen enriched BAC	Mixed textile dyeing–printing (Reactive blue dye) and alkali peeling wastewater	The initial contact bio-film system improved biodegradability while subsequent BAC system, due to enhanced biodegradation induced by high DO level maintained by high pressure (0.4 MPa), achieved high turbidity, colour, COD, & NH3-N removal with concurrent prolonged carbon-bed life, the performance essentially being better than normal BAC or pure GAC process.
Powdered activated carbon or organic flocculant addition in biological system	Cotton textile wastewater	Only bio (SRT = 30 days, HRT = 16 days): 94% COD removal, 36% decolouration. Combined (PAC = 200 mg/L or Organic flocculant = 120 mg/L): Decolouration improved up to 78%, the organic flocculant producing less excess sludge than PAC.
Bio/NF	Diluted wool dyeing bath containing metal complex & acid dye (original dye concentration 8 g/L)	Diluted dye bath (COD = 2 g/L) after activated sludge treatment (COD = 200 mg/L) was subjected to nanofiltration that resulted in reuse standard permeate (further 99% colour & 88% COD removal) with less fouling as compared to that for direct nanofiltration of dye baths. Ozonation of membrane–retentate before recycling to activated sludge process was recommended.

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Table 12.- List of examples of combinations between biological treatment and other technologies (textile wastewater and mixings) (Adapted from Hai et al., 2007) (continuation II)

Technology	Dye/Wastewater	Details
Bio/membrane (+aluminium polychloride)	Domestic + Textile industry (80% by organic load) wastewater	Microfiltration (300,000 D, cross-flow) followed by nanofiltration (150 D, 10 bar, spiral wound) along with aluminum polychloride (70 mg/L) produced recyclable water (COD <10 mg/L, conductivity <40 us/cm, negligible residual colour) from the secondary effluent; alternately "clariflocculation (Dose: 4 ppm, vol.) +multimedia filtration + low-pressure RO (58 D, 4 bar, 10 L/m².h, spiral wound)" seemed preferable in techno-economic analysis.
Bio/NF or O_3	Wastewater from printing, dyeing & finishing textile plant	Biologically treated: Conductivity (mS/cm) 2.8–3.33; COD (mg/L) 200–400. Following biological treatment: i) Nanofiltration (flow rate = 200–400 L/h, TMP = 20 bar): COD <50 mg/L; Conductivity = 0.39–0.51 mS/cm. ii) O_3: COD = 286 (30 min), 70 (210 min) iii) O_3+UV: COD <50 (30 min), <50 (210 min). Ozonized (with/without UV) wastewater can't be reused for rinsing due to negligible conductivity removal although the process is free from reject stream generation.
Bio/NF/O_3	Textile wastewater mixed with domestic (20%) wastewater	Ozonation (12 ppm, 2h) of membrane concentrates (COD = 595, TOC = 190, Conductivity = 5 mS/cm, BOD_5 = 0, EC20 = 34%, pH = 7.9) resulting from nanofiltration (10 bar, 300 L/h) of biologically treated secondary textile effluent achieved 30%, 50%, and 90% reduction in TOC, COD, and toxicity, respectively, making the effluent recyclable to biological treatment.
Bio/NF/ photocatalytic membrane reactor	Textile wastewater	Visible Light mediated Fenton (Nafion-Fe^{+3} membrane, 1.78%; H_2O_2, 10 mM) treatment (3 h) of membrane concentrates (COD = 496, TOC = 110, pH = 8) resulting from nanofiltration of biologically treated secondary textile effluent resulted in 50%, 20–50%, and 50% reduction in TOC, absorbance, and toxicity, respectively. Further degradation through biological treatment possible at low cost due to biocompatible pH of the effluent.
Bio/ clariflocculation/ GAC or bio/membrane (MF→NF)/O_3	Textile wastewater mixed with domestic (25–30%) wastewater	Due to cost of membrane and, COD & salinity increase in biological plant by membrane retentate, techno-economic analysis favoured post treatment of biologically treated effluent by 'clariflocculation followed by GAC adsorption' over 'membrane filtration (MF followed by NF) followed by ozonation', although the latter produced better & constant quality (softened, colourless) recyclable effluent.

Other biological system configurations like biofilm reactors have also been combined with AOPs such as H_2O_2/UV, TiO_2/UV and photo-Fenton to treat reactive azo-dyes, achieving 99% removal efficiency (Sudarjanto et al., 2006; Kim and Park, 2008; García-Montaño et al., 2008a,b).

Finally, membrane bioreactors implementing special dye-degrading microorganisms and involving simultaneous addition of adsorbent in MBR may surface as potential contenders among present-day dye wastewater treatment processes (Hai et al., 2006). The MBR technology may also be combined with advanced oxidation facilities. Case-specific selection of the appropriate hybrid technology is the key to a feasible system.
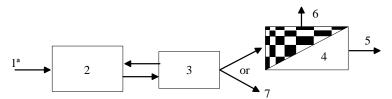

Figure 8.- Integrated MBR-AOP-Membrane treatment scheme. 1. Wastewater[a]; 2. Membrane separated fungi reactor; 3. Solar photocatalytic reactor; 4. RO membrane; 5, 7. Recyclable water; 6. Concentrated salt. [a]For an integrated textile processing plant the wastewater is composed of the concentrate and discarded streams after possible material recoveries, and passes through a treatment route of 2-3-7. For a plant only including dyeing and finishing, the mixed effluent without any attempt of recovery will be fed, and at the end salt and water will be recovered through RO filtration, thereby, involving a treatment route of 2-3-4-5. (Adapted from Hai et al., 2007)

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5.- TRENDS IN THE DEVELOPMENT OF ADVANCED OXIDATION METHODS

Although many of the advanced oxidation processes shown in the following Table 13 have not yet passed the pilot plant development, there are already available technology essentially applicable in industrial effluents. Most systems use proposed O_3/H_2O_2 or are based on the use of ultraviolet radiation methods. Its use is still very limited, and it is subject to the restrictions imposed by industrial discharges competent administration.

Table 13.- Some commercial advanced oxidation processes (Adapted from Rodríguez et al., 2006; Sanz et al., 2013)

Ultrox® Advanced Oxidation Process Ultrox International/U.S. Filter This technology is based on the joint application of hydrogen peroxide, ultraviolet radiation and ozone. This technology is effective for treating organic substances in concentrations lower than 1%, in matrices of low turbidity and low concentrations of carbonate. Startup and operation costs are similar to those of adsorption facility. Fixed cost for treating a phenolic effluent into a timber silver Denver (Colorado, USA) was $ 200,000 and the operation cost of about $ 10.92 per 1000 gallons of water treated.
Rayox® Calgon Carbon Oxidation Technologies It is a photodisinfection and photochemical oxidation process and based on the H_2O_2/UV system that uses the energy of medium pressure UV lamps. Powered by Calgon Oxidation Technologies (Pittsburgh), it has about 350 units in operation. It is able to treat a number of volatile organic compounds (VOCs). Not suitable for high concentrations due to the reagents elevated cost, but is very competitive for a wide range of contaminants at appropriate concentrations. The cost of operation is around 2 to 3 times greater than the active carbon, a suitable option for concentrations below 10 ppm. Operating costs of Rayox® are very low. For example the operator of Salt Lake City water (Utah, USA) has a 360 KW installation for treating tetrachloroethene with an operation cost of $ 0.20 per 1000 gallons of water treated.
Perox-Pure ® Calgon Carbon Oxidation Technologies This system is based on the combination of UV and hydrogen peroxide. It is effective for the treatment of compounds as VOC, polycyclic aromatic, pesticides, among others, at concentrations lower than 500 mg/L. It can be used in combination with other technologies such as air-stripping. Operating costs are high, increasing to factors such as turbidity or retention times. This technology has been used primarily for the treatment of contaminated groundwater. Thus, in the treatment of water containing pentachlorophenol an industry in the State of Washington has estimated a cost of $ 3.90 per 1,000 gallons of water, which included the cost of electricity ($ 2.57), hydrogen peroxide ($ 0.87) and maintenance ($ 0.46).
CAV-OX® process - Magnum Water Technology The CAV-OX® process uses a combination of hydrodynamic cavitation and ultraviolet (UV) radiation to oxidize contaminants in water. The process is designed to remove organic contaminants from wastewater and groundwater without releasing volatile organic compounds into the atmosphere.
HiPOx process The HiPOx process, developed by Applied Process Technologies (California), using O_3/H_2O_2 system to oxidize organic compounds in water using oxygen to generate ozone, thus achieving concentrations of 8-10%, improving mass transfer. The operating pressure is about 2 bar and the system is designed to prevent bromates generation.
WPO process Developed by IDE and INSA (France), it is a process derived from Fenton method. Using hydrogen peroxide as oxidant and a catalyst Fe (II) in an acidic medium. This technology operates at 90-130 ºC and 1-5 bar exceeding a 95% in oxidation efficiencies. The catalyst was recovered by precipitation throuch a pH arise.Several pilot units have been installed in France and Spain.

Major advanced oxidation technologies are actually at development stage. Below are some of the most important research lines determined by investigations in most cases defined as clearly pre-commercials:

Table 14.- Advanced Oxidation Technologies under development (Adapted from Rodríguez et al., 2006)

Development	Applicability
Degradation of emerging trace contaminants	Ozonation processes
In-situ Applications by oxidants injection in groundwater and soil.	Fenton classic
Combination of ultrasound and other oxidation techniques.	Ultrasound techniques.
Development of more stable and efficient anodes.	Anodic oxidation
Non-conventional catalysts development	Catalytic ozonation
Development of catalysts for solar photocatalysis.	Photocatalytic processes
Photoreactors design able to harness solar radiation.	Photocatalytic processes
Advanced oxidation treatments coupled with biological treatments.	All processes

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ANNEX 1
RELATIVE TO AOPs TECHNICS COSTS

The overall costs are represented by the sum of the capital costs, the operating costs, and maintenance costs. Most costs are very site specific, and for a full-scale system these costs strongly depend on the flow rate of the effluent, the configuration of the reactor, the nature (concentration) of the effluent, and the pursued extent of treatment. The location is also important, not only for its obvious influence on land price but also due to its climatic influence, for example, duration and intensity of sunlight influencing efficiency of solar-Fenton process. Table lists some cost values quoted in different studies.

Studies generally show that AOPs and membrane processes are more costly than biological processes. However, because of the numerous site-specific factors and assumptions inevitably made in such estimates, a direct comparison is difficult. Especially, indiscriminate comparison of costs (in per cubic meter or per kilogram contaminant) of segregated versus mixed streams would be simply misleading, as the latter remove significantly less contaminant due to dilution. The fact that treatment schemes based on segregated waste streams coupled with process water recycling have the potential to save quite a bit of money even with high costs per cubic meter should be considered while evaluating process viability. Nevertheless, the importance of reporting such values cannot be overlooked as they always give some rough idea on different scenarios and may as well form the base for further improved cost estimation.

Table A1.1.- Cost information (Adapted from Hai et al., 2007)

Purpose & Technology	Cost	Dye/Wastewater	Remarks
UV/H_2O_2 treatment of secondary textile effluent to meet discharge standard	US$ 0.85 m^{-3}	Textile wastewater	Operating cost including lamp replacement, chemical and electrical cost. (Discharge standard: COD < 100 mg/L; colour < 400 ADMI unit)
Post treatment of secondary textile effluent by (i) ozonation, (ii) membrane filtration	US$ m^{-3} (i) 0.19, (ii) 0.69	Textile wastewater containing direct and reactive dyes	Cost includes both capital & operating cost (except the reject disposal cost in case of membrane filtration). Flow rate, (a) 2000 m^3/d; (b) 1000 m^3/d.
Combined treatment with coagulation/electrochemical oxidation/activated sludge	US$ 0.34 ton^{-1}	Textile wastewater containing 15 dyes used in a plant making primarily cotton and polyester fibres and small quantity of wool	Mainly cost of consumables included. Economical than the conventional treatment process (US$ 0.45 ton^{-1}) used at that time in Taiwan.
Combined treatment with coagulation/Fenton's reagent/activated sludge	US$ 0.4 m^{-3}	Textile wastewater	Running cost, excluding that for sludge disposal. Economical than the conventional treatment process used at that time.
Combined treatment with Coagulation/Activated sludge/ Filtration/Disinfection	US$ 0.19– 0.22 m^{-3}	Textile wastewater	Operating cost (consumables and maintenance)
Combined treatment with bio/sand filter (SF)/O_3 for reusable water	US$ 0.13^{b} m^{-3}	Wastewater from plants dyeing & finishing natural/synthetic fibres	Cost mentioned is for operation & maintenance. Including investment cost, it may amount up to 0.52 US$ m^{-3} depending on amount of water treated, although investment may be repaid in a short time due to saving of cost of water supply (0.52–1.3 US$ m^{-3}).

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Table A1.2.- Cost information (Adapted from Hai et al., 2007) (continuation)

Purpose & Technology	Cost	Dye/Wastewater	Remarks
Combined treatment with bio/ clariflocculation/ GAC for reusable water	US$ 0.454[b] m^{-3}	Textile wastewater mixed with domestic (25–30%) wastewater	Flow rate = 25,000 m^3/d. Cost includes both capital & operating cost.
Combined treatment with bio/ membrane (MF →NF)/O₃ for reusable water	US$ 1.69-1.95[b] m^{-3}	Textile wastewater mixed with domestic (25–30%) wastewater	Flow rate = 25,000 m^3/d. Cost includes both capital & operating cost. The system may potentially become cost-effective with decline in membrane cost, the main cost-contributing factor.
Combined treatment with bio/ sand filtration (SF)/ membrane (UF followed by RO) for reusable water	US$ 1.26[b] m^{-3}	Wastewater from plants dyeing & finishing natural/synthetic fibres	Flow rate = 1000 m^3/d; Cost includes both operating and investment costs.
Combined treatment with deep aeration activated sludge/ BAC/membrane (NF) for 50% recycling	US$ 0.294[C] m^{-3}	Wastewater from plants dyeing & finishing synthetic fibres	Flow rate = 50 m^3/d; Cost mentioned is for operation & maintenance.
Combined treatment with bio/sand filtration (SF)/ ozonation for 50% recycling	US$ 0.57[b] m^{-3}	Wastewater from plants fulling & dyeing natural/synthetic fibres	Flow rate = 2000 m^3/d; Operating cost only. Required fresh water supply (50% of total) incurs a further cost of 0.92 US$ m^{-3}.
Reuse after membrane filtration (i), followed by UV/H2O2 (ii), concurrent with reuse after membrane concentrate treatment by wet air oxidation (iii) and biological (iv)	US$ m^{-3} (i) 0.53 (ii)2.6 (iii)4.4 (iv)0.13	Textile wastewater	Flow rate = 400 m^3/d. Indicated costs are operating and maintenance costs for each stage of the integrated system. Annualized total installation cost is US$ 243,000 while saving generated from water reuse is US$ 98,000.
Membrane bioreactor	US$ 0.273 m^{-3}	Municipal wastewater [d]	Flow rate = 2.4 m^3/h; cost mentioned includes all sorts of capital & operating costs. With expected decline in membrane cost to US$ 50 m^{-2} in 2004, the unit cost would reduce to US$ 0.181 m^{-3}.

[a,b,c] Original reported values in Deutsche Marks, Euro and Taiwanese dollar have been converted to US$ by multiplying with a factor of 0.663348, 1.29730, 0.0322134, respectively. [d]Data given for comparison of MBR technology with others only.