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## Hybrid treatment systems for dye wastewater

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### Abstract

Virtually all the known physico-chemical and biological techniques have been explored for treatment of extremely recalcitrant dye wastewater; none, however, has emerged as a panacea. A single universally applicable end-of-pipe solution appears to be unrealistic, and combination of appropriate techniques is deemed imperative to devise technically and economically feasible options. An in-depth evaluation of wide range of potential hybrid technologies delineated in literature along with plausible analyses of available cost information has been furnished. In addition to underscoring the indispensability of hybrid technologies, this paper also endorses the inclusion of energy and water reuse plan within the treatment scheme, and accordingly proposes a conceptual hybrid dye wastewater treatment system.

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# Hybrid Treatment Systems for Dye Wastewater

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## Abstract:

*Virtually all the known physico-chemical and biological techniques have been explored for treatment of extremely recalcitrant dye wastewater; none, however, has emerged as a panacea. A single universally applicable end-of-pipe solution appears to be unrealistic, and combination of appropriate techniques is deemed imperative to devise technically and economically feasible options. An in-depth evaluation of wide range of potential hybrid technologies delineated in literature along with plausible analyses of available cost information has been furnished. In addition to underscoring the indispensability of hybrid technologies, this paper also endorses the inclusion of energy and water reuse plan within the treatment scheme, and accordingly proposes a conceptual hybrid dye wastewater treatment system.*

**KEY WORDS:** dye wastewater, decolorization, hybrid treatment systems, energy and water reuse.

## I. INTRODUCTION

Large amounts of dyes are annually produced and applied in many different industries, including the textile, cosmetic, paper, leather, pharmaceutical and food industries.<sup>136</sup> There are more than 100,000 commercially available dyes with an estimated annual production of over  $7 \times 10^5$  tons<sup>179</sup>, fifteen percent of which is lost during the dyeing process.<sup>70</sup> The textile industry accounts for the two-third of the total dyestuff market<sup>136</sup> and consumes large volumes of water and other refractory chemicals for wet processing of textiles<sup>210</sup>. The chemical reagents used are very diverse in chemical composition, ranging from inorganic and low molecular weight organic compounds to polymers.

The presence of even trace concentration of dyes in effluent is highly visible and undesirable.<sup>79</sup> The release of colored wastewater in the ecosystem is a remarkable source of esthetic pollution, eutrophication and perturbations in aquatic life.<sup>70</sup> Dye effluent usually contains chemicals, including dye itself, which are toxic, carcinogenic, mutagenic, or teratogenic to various microbiological and fish species.<sup>50</sup> Concern arises, as many dyes are made from

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known carcinogens such as benzidine and other aromatic compounds.<sup>179</sup> Also azo- and nitro-compounds have been reported to be reduced in sediments of aquatic bodies, consequently yielding potentially carcinogenic amines that spread in the ecosystem.<sup>211</sup> The presence of dyes or their degradation products in water can also cause human health disorders such as nausea, hemorrhage, ulceration of skin and mucous membranes<sup>195</sup>, and can cause severe damage to kidney, reproductive system, liver, brain and central nervous system.<sup>94</sup> These concerns have led to new and/or stricter regulations concerning colored wastewater discharges, compelling the dye manufacturers and users to adopt “cleaner technology” approaches, for instance, development of new lines of ecologically safe dyeing auxiliaries and improvement of exhaustion of dyes on to fiber.<sup>79, 180, 210</sup>

Concomitant with the in-house multi-dimensional pollution minimization efforts, a number of emerging material recovery/ reuse and end-of-pipe decolorization technologies are being proposed and tested at different stages of commercialization. However, due to their synthetic origin and complex structure deriving from the use of different chromophoric groups, dyes are extremely recalcitrant.<sup>179</sup> Along with the recalcitrant nature of dye wastewater, the frequent daily variability of characteristics of such wastewater adds to the difficulty of treatment.<sup>77</sup> Accordingly, despite the fact that virtually all the known physico-chemical and biological techniques have been explored for decolorization,<sup>79</sup> none has emerged as a panacea. Cost-competitive biological options are rather ineffective while physico-chemical processes are restricted in scale of operation and pollution profile of the effluent. Table 1 lists the advantages and disadvantages of different individual techniques. It appears 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. In light of this researchers have put forward a wide range of hybrid decolorization techniques. Figure 1 depicts a simplified representation of the proposed combinations.

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 physico-chemical treatments, which often have been employed by industries in simple, standalone manner. Combinations of conventional physico-chemical 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 physico-chemical and advanced oxidation processes.

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This paper offers a comprehensive review of the potential hybrid technologies delineated in literature for treatment of dye wastewater in general and textile wastewater in particular. Analogous to the aforementioned trends, the combinations have been outlined under three broad categories i.e., combination among AOPs, combination of physico-chemical treatments among themselves and those with the AOPs and, the one with the paramount importance, the combination of biological systems with conventional physico-chemical processes and AOPs (Fig.1). Before elaborating on the combinations, the basic principles and limitations of relevant individual techniques have been 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.

## II. 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.<sup>72,73</sup> These processes are cost prohibitive and complex at the present level of their development.<sup>163</sup> 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.<sup>11,149,152</sup> 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 case of photochemical/ photocatalytic decoloration, most of the investigations involve reactors ranging from as small as few tens of milliliters (e.g., 40 ml<sup>38</sup>) to several hundreds of milliliters (e.g., 250ml<sup>146</sup>) or at best few liters (e.g., 4L<sup>64</sup>), which are inadequate to explicitly address the light penetration issue, the inherent drawback of this technology. Only a handful of pilot plant explorations with less than persuasive<sup>192,193</sup> or moderate<sup>187</sup> 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 decolorization. The conventional oxidants have more significant thermodynamic and kinetic limitations.<sup>46</sup> For the AOPs, the basic reaction mechanism is the generation of free radicals and subsequent attack by these on the pollutant

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organic species. Hence it is strongly believed that their combination will result in more free radicals, thereby increasing the rates of reactions.<sup>72,73</sup> 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. Table 2 furnishes 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.

### **A. 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 UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide<sup>4</sup>, ozone<sup>39</sup> or Fenton's reagent<sup>152</sup> has been frequently reported to be superior to sole 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<sup>192</sup> and/or a specifically designed reactor.<sup>119</sup> One example of appropriate reactor is a reactor which 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.<sup>187</sup> Arslan et al.<sup>8</sup> proposed pre-ozonation to remove high UV-absorbing components, and thereby accelerate subsequent H<sub>2</sub>O<sub>2</sub>-UV treatment by increasing UV-penetration. Simultaneous use of UV/H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> has also been reported to yield enhanced reaction kinetics.<sup>12</sup> However, this entailed additional cost as compared to UV/ H<sub>2</sub>O<sub>2</sub> or UV/O<sub>3</sub>, and hence such use is recommended to be weighed against degree of removal required and associated cost. As activator of oxidants like O<sub>3</sub> or H<sub>2</sub>O<sub>2</sub>, handful of studies have put forward other alternatives to UV, namely, reduced transition metals<sup>9</sup>, gamma irradiation<sup>80,194</sup>, humic substances<sup>82</sup> etc.

An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors i.e., heterogeneous photocatalysis. Various chalcogenides (oxides such as TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, CeO<sub>2</sub> etc. or sulfides such as CdS, ZnS etc.) have been used as photo-catalysts so far in different studies. However, titanium dioxide (TiO<sub>2</sub>) in the anatase form is the most commonly used photocatalyst, as it has reasonable photoactivity.<sup>143</sup> Moreover it also furnishes the advantages of being insoluble, comparatively inexpensive, non-toxic, together with having resistance to photocorrosion and biological immunity.<sup>6</sup> The photocatalytic process can be carried out by simply using slurry of the fine catalyst particles

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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 requirement of 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  $O_3$ <sup>146</sup> or  $H_2O_2$ <sup>200</sup>, exhibiting enhanced decoloration and mineralization, are also available. Considering the total mineralization of the compounds, the photocatalytic ozonation (UV/ $O_3$ /TiO<sub>2</sub>) may show much lower specific energy consumption than the conventional photocatalysis (UV/TiO<sub>2</sub>) and ozonation (UV/ $H_2O_2$ / $O_3$ ).<sup>106</sup>

Fenton reagent (a mixture of  $H_2O_2$  and  $Fe^{2+}$ ) and its modifications such as thermal Fenton process<sup>201</sup> or photo-Fenton reaction using Fe(II)/Fe(III) oxalate ion,  $H_2O_2$  and UV light have received great attention as means for decolorization of synthetic dyes.<sup>190,202</sup> In the case of photo-Fenton technique,  $H_2O_2$  is utilized more rapidly by three simultaneous reactions namely direct Fenton action, photo-reduction of Fe(III) ions to Fe(II) and  $H_2O_2$  photolysis. Thus this process produce more hydroxyl radicals in comparison to the conventional Fenton method or the photolysis.<sup>20,73</sup> 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.<sup>24</sup> However Fenton reagent necessitates use of a large amount of acidic and alkaline chemicals (ideal pH about 2.5). Compared to Fenton's reagent,  $\beta$ -FeOOH catalyzed  $H_2O_2$  oxidation process takes advantage of its applicability over a wider pH range between 4 to 8, and moreover no sludge is produced.<sup>107</sup> 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 ' $H_2O_2$ / 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.<sup>203</sup> 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.<sup>211,212</sup>

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Among the AOPs, the photo-Fenton reaction<sup>207</sup> and the TiO<sub>2</sub> mediated heterogeneous photocatalytic treatment<sup>38</sup> 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.<sup>7</sup> Recently, several attempts have been made to increase the photocatalytic efficiency of TiO<sub>2</sub>; these include noble metal deposition, ion doping, addition of inorganic co-adsorbent, 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<sub>2</sub> is only about 3%.<sup>38</sup>

## **B. 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.<sup>40</sup> 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 COD removal<sup>6</sup> and added advantage may be derived from existence of salt in solution, which originally is detrimental for sole photocatalysis.<sup>238</sup> Conversely, electro-Fenton process requires no addition of chemical other than catalytic quantity of Fe<sup>+2</sup>, since H<sub>2</sub>O<sub>2</sub> is produced in situ, thereby avoiding transport of this hazardous oxidant.<sup>76,154</sup> In pulsed high voltage electric discharge process, addition of oxidants such as H<sub>2</sub>O<sub>2</sub> yields highly reactive free radical species through photo-dissociation of H<sub>2</sub>O<sub>2</sub> and thereby enhances the whole process.<sup>200</sup>

## **C. Sonolysis and other AOPs**

Acoustic cavitation due to ultrasound vibration within a liquid generates local sites of high temperature and pressure for short period of time, which gives rise to H<sub>2</sub>O 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<sup>73</sup>. In view of the substantial amount of energy employed in generating free radicals via acoustic

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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 photo-catalyst owing to adsorption of contaminants at the surface. On the other hand, such combination can alleviate the limitations of separate application of sonolysis.<sup>148,198</sup> Similar advantage has been reported in case of concurrent sonolysis and MnO<sub>2</sub> oxidation.<sup>68</sup> Sonification has also been reported to bring about dramatic enhancement in oxidation efficiency of UV/H<sub>2</sub>O<sub>2</sub> by improving oxygen uptake and transfer.<sup>63,64,216</sup> Combined application of sonolysis and O<sub>3</sub>/UV facilitates O<sub>3</sub> diffusion and photolysis of ultrasound-generated H<sub>2</sub>O<sub>2</sub>.<sup>53,90,206</sup> Such combination hence yields large number of free radicals. Addition of FeSO<sub>4</sub> in solution may result in Fenton's reaction with H<sub>2</sub>O<sub>2</sub> evolved from simultaneous sonification and may achieve improved decoloration and TOC removal as compared to sonification only.<sup>93</sup> Simultaneous sonolysis has also been reported to enhance electro-oxidation of dye.<sup>135</sup>

### III. COMBINATION: AOPs AND OTHER PHYSICO-CHEMICAL 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. Table 3 encapsulates information derived from broad spectrum of typical studies dealing with such combinations.

#### A. 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 decolorization. Their stand alone application in treating textile/dye waste is, however, relatively ineffective<sup>79,101,163</sup>, for example, only 50% removal was achieved using either alum or ferrous sulfate for an azo reactive yellow dye.<sup>79</sup> 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.<sup>179</sup>

Nevertheless, researchers are persistent in their pursuit of minimizing the limitations of this technology. For instance, Polyaluminium 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 decoloration capacity surpassed that of Poly aluminium chloride and Polyferric sulfate.<sup>66</sup> On the other hand, to avoid massive sludge

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disposal problem, different novel approaches, such as, coagulation of low volume segregated dye bath (rather than that of colossal amount of mixed wastewater)<sup>74</sup>, alum sludge recycling<sup>41</sup>, coagulant recovery from textile chemical sludge<sup>122</sup>, reuse of textile sludge in building materials<sup>16</sup>, and processes like vermicomposting of textile mill sludge<sup>67</sup>, coagulation followed by activated carbon adsorption<sup>163</sup>, 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.<sup>163</sup>

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 standalone applications.<sup>101</sup> One of the limitations of Fenton oxidation process is that, large amounts of small, hard to settle flocs are consistently observed during the process. Chemical coagulation following Fenton's treatment has been found to reduce floc-settling time, enhance decoloration and reduce soluble iron in effluent.<sup>131</sup> Conversely photo-Fenton process subsequent to coagulation was reported to complete decoloration and yield better COD removal, with the added advantage of reducing load on the advanced oxidation process, thereby reducing chemical usage.<sup>18</sup> Investigation on sequential use of coagulation and ozonation revealed the superiority of the scheme involving ozonation preceded by coagulation over the reversed scheme.<sup>209</sup> Multistage application of coagulation followed by ozonation was proved to be superior to their single pass sequential application (total ozonation time the same)<sup>86</sup>. The advantage of the multistage application was more convincing in case of wastewater with more recalcitrant composition.

## **B. Adsorption based combinations**

Adsorption techniques, specially the excellent adsorption properties of carbon-based supports have been utilized for the decolorization of dyes in the industrial effluents.<sup>60</sup> 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.<sup>137</sup> It is very effective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes<sup>179</sup>. However, the use of carbon adsorption for decolorization of the raw wastewater is impractical because of competition between colored 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 color standards.<sup>79</sup> The fact that activated carbon is

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expensive and weight loss is inevitable during its costly onsite regeneration (10% loss in the thermal regeneration process)<sup>99</sup>, impedes its widespread use. Utilization of non-conventional, 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.<sup>142,181</sup>

There has been considerable interest in using low-cost adsorbents for decolorization of wastewater. These materials include chitosan, zeolite, clay; certain waste products from industrial operations such as fly ash, coal, oxides; agricultural wastes and lignocellulosic wastes and so on.<sup>14,151</sup> Each of 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.<sup>99</sup>

As mentioned earlier, adsorption is a non-destructive 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 pre-concentrated on adsorbent and then separated from water. The contaminants thus separated may subsequently be mineralized, for example, by wet air oxidation<sup>191,223</sup> or degraded to some extent, for instance, azo bond reduction by bisulfite-mediated borohydride<sup>117</sup> 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 et al.<sup>89</sup> proposed a slightly modified version of the aforementioned so called “phase-transfer oxidation”. Their strategy comprised of simultaneous operation of adsorption and AOP followed by periodic on-site destructive regeneration of the spent adsorbent. Adsorption concurrent with ozonation<sup>132</sup>, UV-H<sub>2</sub>O<sub>2</sub><sup>91</sup> or microwave induced oxidation<sup>132</sup> 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.<sup>87,150</sup> 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.

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### C. Membrane based combinations

Membrane separation endows the options of either concentrating the dyestuffs and auxiliaries and producing purified water<sup>208</sup>, or removing the dyestuff and allowing reuse of water along with auxiliary chemicals<sup>110,172,174</sup>, or even realizing recovery of considerable portion of dye, auxiliaries and water all together.<sup>171</sup> Such recovery/ reuse practice reduces many folds the recurring cost for the treatment of waste streams. The fact that the dyeing behavior of the residual dye should ideally be identical to that of the fresh dye, may restrict dye recovery and reuse to specific dye classes.<sup>35,65</sup> 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<sup>36</sup>. Two distinct trends are hence noticeable among the reported studies which 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 photocatalyst<sup>145</sup>. 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.<sup>204</sup> proposed a photo-oxidative (UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>) pretreatment prior to membrane filtration to partially break down the high molecular weight compounds which cause membrane fouling. The relatively smaller fragments produced there from 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<sup>2</sup>/m<sup>3</sup>H<sub>2</sub>O for hollow fiber membranes), easy scale-up, no foam formation, and lower process cost (no requirement of ozone destruction, lower ozone loss).<sup>42,45</sup>

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Numerous studies have reported on application of membrane filtration (UF/NF) following coagulation/ flocculation to produce reusable water.<sup>25,26,139</sup> Such application has the added advantage of minimizing membrane fouling. In this context, 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.<sup>88</sup>

Application of separate technologies for segregated streams has been recommended by different researchers. For instance, Wenzel et. al.<sup>219</sup> 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, 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.<sup>168</sup>

Considerable number of studies have been devoted to eradication of the major drawback associated with membrane separation i.e., concentrated residue remaining for disposal. As mentioned earlier, dyes in the concentrate from the membrane separation unit, because of the usual quality requirements of the color 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.<sup>55,118</sup> Sonification was found essential to make membrane-retentate from actual wastewater to be amenable to subsequent WAO.<sup>54</sup> 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.<sup>222</sup> A novel membrane-based integrated water management system for exhausted dye bath and rinsing bath was proposed by Bruggen et al.<sup>34</sup> 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.

#### IV. BIOLOGICAL TREATMENT BASED COMBINATIONS

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## A. Combination among biological processes

Conventionally a chemical coagulation step, preceded by<sup>229</sup> or antecedent to<sup>57</sup> biological treatment, is applied for dye wastewater. Combined treatment with municipal wastewaters is usually favored<sup>75</sup> wherever applicable. A variety of biological treatment processes including activated sludge, fluidized biofilm<sup>229</sup>, different fixed film systems<sup>3</sup> or combinations thereof<sup>230</sup> have been employed. Although in case of aerobic bacteria co-metabolic 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 condition.<sup>19,199</sup> 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 color in discharged effluents.<sup>160</sup>

Since reduction of azo bond can be achieved under the reducing conditions prevailing in anaerobic bioreactors<sup>31</sup> and the resulting colorless aromatic amines may be mineralized under aerobic conditions<sup>32</sup>, so a combined anaerobic-aerobic azo dye treatment system appears to be attractive. Trials with varieties of combinations including simultaneous anaerobic/ aerobic process (microbial immobilization on a matrix providing oxygen gradient<sup>113</sup> or an anaerobic-aerobic hybrid reactor<sup>95</sup>), anoxic plus anaerobic/ aerobic process<sup>162</sup>, anaerobic/ oxic system<sup>5</sup>, aerobic (cell growth)/ anaerobic (decolorization) system<sup>37</sup> have all been explored involving fed-batch, sequencing batch or continuous feeding strategies with encouraging results. Both cytoplasmic<sup>184</sup> and membrane<sup>114</sup>-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 color removal.<sup>52</sup> Different abiotic processes involving derivatives generated during bacterial metabolism (e.g., sulfide, amino acid cysteine, ascorbate) may contribute in decolorization under anaerobic conditions<sup>227</sup>. The biotic process, however, dominates in high-rate anaerobic bioreactors.<sup>233</sup> Addition of redox mediating compounds like anthraquinone sulphonate, anthraquinone di-sulphonate has been reported to greatly enhance both the biotic and abiotic processes<sup>233</sup>. 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 colored

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but also because some of these compounds, e.g., azoxy compounds, may cause toxicity.<sup>232</sup> 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 afterwards in order to achieve nitrogen removal.<sup>52</sup>

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 such innovative endeavors include- two stage activated sludge process (high load first stage, achieving biosorption and incipient decomposition of high molecular organic compounds, followed by a low load polishing stage)<sup>104</sup>; high-rate anaerobic systems uncoupling hydraulic retention time from solids retention time<sup>125</sup>; two phase anaerobic treatment wherein acidic phase bioreactor is also shared for textile production (integration of production with wastewater treatment)<sup>59</sup>; activated sludge pretreatment, to reduce organic nitrogen, before fungi decoloration<sup>144</sup>; fungi pretreatment before anaerobic treatment<sup>58</sup>; combined fungi (biofilm) and activated sludge culture<sup>98</sup> for decoloration; activated algae reactor (with mixed population of algae and bacteria)<sup>13</sup>; activated sludge followed by over land flow<sup>185</sup> etc.

## **B. Hybrid technologies based on biological processes**

Table 4 summarizes a broad spectrum of intriguing reports on hybrid technologies having biological processes as the core.

### **1. Biological/ Physico-chemical**

As mentioned earlier, literature is replete with examples of use of coagulation complementary to biological decoloration. The choice between coagulation-biological or biological-coagulation scheme depends on type and dosage of coagulant, sludge quantity, and degree of inhibitory and nonbiodegradable substances present in wastewater. Coagulation prior to biological treatment may be advantageous for alkaline wastewaters. After biological treatment ferrous sulfate cannot be used because pH is close to neutral. On the other hand, the dose of coagulants and consequently the quantity of the chemical sludge after biological treatment are smaller compared to those in coagulation followed by biological treatment.<sup>57,75,100</sup>

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Besides coagulation, a variety of other treatment processes may be combined with biological treatment. Very often certain physico-chemical process is placed before<sup>129</sup> and/or after<sup>130</sup> an advanced oxidation process. The biological process is applied either as the very first<sup>100</sup>, penultimate<sup>3</sup> or as the last<sup>129</sup> treatment unit. In view of the abundance of bioresistant and toxic contaminants in dye wastewater, physico-chemical and advanced oxidative pretreatment prior to biological treatment appear to be a rational option. The choice between physico-chemical and oxidative pretreatment however depends on the specific wastewater; and usually an astute stream-separation would facilitate application of appropriate treatment system for different streams.<sup>3</sup> On the contrary, especially isolated/ acclimatized microbes are usually required for effective biological pretreatment.<sup>100,115</sup> In order to obtain reusable water, an elaborate treatment train composed of conventional physico-chemical and advanced oxidation processes may be placed after biological pretreatment. While numerous such combinations have been reported in literature, the common underlying principle is to choose a combination so as to furnish a complete system eliminating limitations of the individual techniques. For instance, the fact that high concentrations of suspended or colloidal solids in the wastewater may impede the advanced oxidation processes, necessitates sufficient prior removal of these materials by physico-chemical treatment.<sup>43,100</sup> Conversely, enhancement of COD removal (e.g., after ozonation)<sup>127</sup> or improvement of settleability of sludge (e.g., after electrofloatation)<sup>43,130</sup> may require physico-chemical treatment subsequent to AOPs.

## 2. Integrated Partial oxidation/ Biodegradation

In contrast to the conventional pre or post treatment concepts, where process design of different components is 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.<sup>134</sup> 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 the 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<sup>39</sup>, H<sub>2</sub>O<sub>2</sub><sup>46</sup>, photocatalysis<sup>178</sup>, photo (solar)-fenton<sup>207</sup>, wet air oxidation<sup>169</sup>, combined photocatalysis and ozonation/ H<sub>2</sub>O<sub>2</sub><sup>146,200</sup>, photoelectrochemical process<sup>6</sup>, sub and super critical water oxidation<sup>103</sup> and electron-beam treatment.<sup>81</sup> Bulk of such studies report on improvement of biodegradability (as revealed by BOD/COD ratio or partial oxidation parameter<sup>92</sup>) and reduction of toxicity (using bioassay, e.g., bioluminescence

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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 table.4, are also available. Careful consideration of characteristics of each AOP would facilitate selection of a proper pre-oxidation process for rendering wastewater more amenable to biological treatment. For instance, Fenton-like treatment using Nafion-Fe<sup>+3</sup> membrane, rather than direct addition of iron salt<sup>17</sup>, or immobilized TiO<sub>2</sub> photocatalysis rather than photo-Fenton process<sup>164</sup> would facilitate further biological treatment under biocompatible pH making neutralization redundant. Mantzavinos et al.<sup>138</sup> 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 results in an increasing mineralization of low molecular weight biodegradable substances.<sup>92</sup> Hence it is rational to adopt shortest possible pre-oxidation 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.<sup>170</sup> An internal recycle between the oxidation and biological stage have been recommended for reducing chemical dose in such circumstances.<sup>124</sup> Dogruel et al<sup>56</sup>, pointed out 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 dye house prior to biological treatment of the mixed whole effluent. If considerable amount of biodegradable compounds originally exist in the wastewater, pre-oxidation step obviously will not lead to a significant improvement of biodegradability, rather 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.<sup>85,213</sup>

### 3. Biodegradation/ Adsorption

Owing to limited effectiveness of conventional biological treatment for recalcitrant textile wastewater composed of recalcitrant textile chemicals and dyes, various adsorbents and chemicals<sup>161</sup>, predominantly activated carbon, have been directly added into the activated sludge systems in certain studies. The fact that the additional removal of soluble organic

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matter (COD and TOC) in such a system over that in a conventional system cannot be explained by probable contribution of adsorbent as predicted by adsorption isotherms<sup>141</sup>, has persuaded researchers to hypothesize a synergistic relationship between activated carbon and microorganism ('enhanced microbial degradation and bioregeneration of adsorbent').<sup>167</sup> Enhanced biodegradation has been attributed to ability of adsorbent to act as a modulator, by immediately adsorbing high concentrations of the toxic compounds, and thus regulating the concentration of the free toxic material; together with providing an enriched environment for microbial metabolism on the liquid-solid surface, on which microbial cells, enzymes, organic materials and oxygen are adsorbed.<sup>1</sup> Conversely, bioregeneration of activated carbon has been explained by extracellular biodegradation of adsorbed organics by microbial enzymes excreted into carbon micropores.<sup>197,225</sup> The main step in dye removal for activated carbon amended biological process is microbial degradation, which is higher than adsorption on both activated carbon as well as on biomass.<sup>49</sup> Accordingly although the dye removal in that process has frequently been reported to be better than in the conventional activated sludge process<sup>161,197</sup>, mode of COD removal may be the same.<sup>49</sup> Under a higher biomass concentration (> 3g/l), the carbon particles are, however, trapped in the floc matrix and lose their properties of adsorption, thereby, hindering microbial growth and dye removal.<sup>141</sup> Although simultaneous adsorption and biodegradation treatment occasionally has been demonstrated as a mere combination of adsorption and biodegradation without any mutual enhancement<sup>159</sup> and has controversies in bioregeneration hypothesis<sup>225</sup>, application of this process to the treatment of textile wastewaters is an important economic improvement. It allows the removal of COD and color from textile wastewater in a single step with no additional physicochemical treatment<sup>141</sup>. To minimize reactor volume, a hydraulic retention time as low as possible is practically expected. This, in turn, however, renders powdered activated carbon (PAC) partially loaded. Its optimum use may be realized by recirculation of PAC.<sup>156</sup> In addition to its adsorption capacity, activated carbon has also been reported to enhance anaerobic azo dye reduction<sup>234</sup> by acting as a biologically regenerable redox mediator due to quinone surface group on it. Zhang et al.<sup>235</sup> documented an innovative approach involving fluidized bed reactor containing complex pellets of white rot fungus and activated carbon. The reactor, by retaining necessary fungal metabolites, surpassed standalone application of fungi or activated C. The process was claimed to be superior to simple addition of activated C in fungi reactor.

Fixed granular activated carbon (GAC) bed inoculated with special chromophoric bond-cleaving and aromatic ring-cleaving bacteria, after initial acclimatization period, have been reported to outperform conventional GAC bed.<sup>218</sup> However, the bacterial activity in GAC bed may decrease after certain period due to lack of nutrient and/or dissolved oxygen.

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Maintenance of high DO level by a pressurized system may ensure achievement of stable removal (color and COD) with concurrent prolonged carbon-bed life.<sup>177</sup> A novel approach entailing partial bioregeneration (physical adsorption on fluidized biological GAC followed by biodegradation and desorption), coupled with complementary periodic physical regeneration of 50% of total GAC, has been reported by Vuoriranta et al.<sup>217</sup> The system was observed to achieve an improved COD and color removal apart from reduction in regeneration cost and weight loss of GAC. Moreover, the system has the added advantage of allowing biological activity in GAC medium for subsequent use. Some means of improvement of biodegradability, be it biological<sup>177</sup> or advanced oxidation process<sup>221</sup>, will certainly fortify biological activity in the subsequent biological GAC. However, in case of oxidative degradation, subsequent substrate adsorption on carbon may plummet<sup>23</sup>. Carbon-biocatalyst amalgamation in adsorption cartridges for decoloration has been commercialized ('BIOCOL') in UK.<sup>48</sup>

#### **4. Biodegradation/ Membrane filtration**

##### **a. Chronological application**

For reusable water production, researchers have recurrently referred to nanofiltration (or low pressure reverse osmosis) of biologically treated colored wastewater since this option involves less fouling as compared to that for direct nanofiltration of dye baths.<sup>33</sup> Some references have put forward inclusion of sand filtration/ multimedia filtration and/or microfiltration in between biological treatment and nanofiltration<sup>139,182</sup>. Site-specific techno-economical analysis is usually recommended to ascertain the best combination<sup>183</sup>. Notwithstanding the disposal problem of reject stream emanating from membrane separation, it may be preferred to ozonation as a post treatment to derive reusable water from secondary wastewater, in view of the fact that the latter would realize negligible conductivity removal.<sup>27</sup> Conversely, provision of advanced oxidation of biologically treated wastewater before sending it for nanofiltration has been reported to yield further increased membrane life.<sup>28,96</sup> Addition of facility for partial oxidative degradation (e.g., ozonation) of membrane-concentrate to the aforementioned treatment train of nanofiltration of secondary wastewater may furnish a quasi-'close loop' system, in that, the partially oxidized products (detoxified) may be recycled to biological treatment.<sup>120,134</sup> Such practice may, however, give rise to concern about salinity increase in biological plant. Wu et al.<sup>224</sup> reported a cost-competitive dye wastewater reclamation system involving deep aeration activated sludge prior to bio-activated carbon and nanofiltration, which, in addition to yielding prolonged membrane life and recovery/reuse potential, allowed direct discharge of concentrated membrane-retentate.

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Illustrations of chronological application of membrane and biological treatment in case of segregated textile wastewater streams are also available. Rinsing water may be reused after reclamation by membrane while the concentrated waste may be degraded in anaerobic digester.<sup>219</sup> This example may be further extended to filtration of segregated dye bath effluent utilizing membrane of appropriate molecular cut off size which allows passage of salt but retains dye. Consequently dye bath water containing salt may be reused for dye bath reconstruction, while the membrane- concentrate may be degraded in anaerobic digester.

### **b. Membrane bioreactors**

Membrane bioreactor (MBR), a remarkable improvement over the conventional activated sludge treatment<sup>214</sup>, has been set forth as a promising option in colored wastewater treatment. MBR for decoloration has often been envisioned in conjunction with simultaneous adsorption.<sup>189</sup> A treatment scheme comprising activated carbon amended anaerobic reactor preceding aerobic MBR realizes stable decoloration along with high TOC removal, with concurrent improvement in activated sludge dewaterability and reduction in filtration resistance.<sup>157</sup> For reuse purpose MBRs have occasionally been envisaged as the main treatment process prior to a polishing nanofiltration step<sup>188</sup>, or even as the core of a rather elaborate treatment train including anaerobic/ aerobic pretreatment prior to MBR and ozonation following it.<sup>112</sup> An innovative approach noticeable in contemporary literatures involves membrane (submerged<sup>78</sup>/ sidestream<sup>62,102</sup>) separated fungi reactor which couples the excellent degradation capability (due to non-specific extracellular oxidative enzymes) of white-rot fungi with the inherent advantages of membrane bioreactor. The MBR system has been envisaged to be capable of coping with the impedances in implementation of white-rot fungi in large scale industrial waste treatment, such as, rather slow fungal degradation<sup>147</sup>, loss of the extracellular enzymes and mediators with discharged water<sup>235</sup>, and excessive growth of fungi<sup>236</sup>. Development of such a system offering stable 99% decoloration and 97% TOC removal from synthetic textile wastewater along with avoidance of membrane fouling has been recently documented.<sup>78</sup>

## **V. COST ANALYSIS**

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 as well as 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

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influence, for example, duration and intensity of sunlight influencing efficiency of solar-fenton process.<sup>187</sup> Table 5 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 m<sup>3</sup> or per kg contaminant) of segregated vs. mixed streams would be simply misleading as the latter removes 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 m<sup>3</sup>, should be considered while evaluating process viability.<sup>124</sup> 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. Plausible analyses of the cost data follow in the next paragraph.

Treatment trains composed of conventional physico-chemical and biological systems involve sustainable cost<sup>155</sup>, however, their removal performance may not satisfy contemporary stricter regulations. Membrane filtration of biologically pretreated dye wastewater<sup>109</sup> has been occasionally reported to require less cost than that for direct membrane filtration<sup>108</sup> of dye bath, presumably as the former involves less membrane fouling. However, both the processes furnish potential of water reuse, thereby, achieving further cost savings. Membrane based other combinations, especially, membrane bioreactor<sup>78,228</sup>, are potential contenders among present-day dye wastewater treatment processes. At the present stage of development of AOPs, sole application of AOP or even combinations among AOPs themselves are unlikely to yield satisfactory effluent with reasonable cost.<sup>12</sup> AOP pretreatment prior to biological treatment is certainly cost-effective than complete mineralization by AOP. Conversely, according to the examples in Table 5, AOP as a post treatment incurs less cost as compared to that as pre-treatment.<sup>109,187</sup> Notwithstanding this fact, it should be emphasized that application of AOP pretreatment on segregated recalcitrant stream may avoid unnecessary consumption of chemicals by biodegradable compounds, thereby, imparting cost-effectiveness to the integrated system.<sup>124</sup> Combination of AOP with adsorption<sup>91</sup>, membrane separation<sup>139</sup> or other physico-chemical<sup>86</sup> systems may be cost-competitive. It is intriguing to notice that integrated systems combining wide variety of technologies, for instance, membrane, AOP, WAO and biological process, when accomplish water and/or auxiliary chemicals reuse, appear to be feasible, in that, capital cost can be recovered within a few years.<sup>43,120,139</sup>

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## VI. PROPOSED HYBRID PROCESS

Based on the array of potential hybrid technologies and the available cost information, a conceptual on-site textile dye wastewater treatment system, as presented in figure 3, may be proposed. Two distinct cases have been considered here- i) an integrated textile processing plant involving essentially all steps of textile processing, starting from conversion of fiber to cloth and extending up to dyeing and finishing, and, ii) a segregated plant concerning only dyeing and finishing. Additionally, an ideal state of practice of recovery and reuse of textile chemicals (sizing agent, detergent, lanolin from raw wool scouring, caustic for cotton mercerizing, dye bath electrolyte), energy (heat) and water by using appropriate membranes has been assumed (Fig.2). This assumption was prompted by the fact that such practice realizes cost-savings through reduction in production of waste and consumption of fresh chemicals/water, and consequently the usual payback period of the high capital investment associated with it is 2-3 years or less.<sup>151,180</sup> Furthermore, available technoeconomical analyses indicate that inclusion of comprehensive energy and water reuse plan within the treatment scheme would be more viable as compared to full end-of-pipe treatment with limited or no recovery/reuse strategy.<sup>51</sup> Nevertheless, initial investment costs and site-specific conditions will obviously play a role in whether or to what extent a plant decides to proceed with recycling concept. It is worth mentioning here that recovery/ reuse of both chemicals and water is different from that of only water, in that, the former entails handling of the point sources separately, while the latter may be achieved by following usual end-of-pipe strategy (mixing different streams).

A submerged microfiltration membrane bioreactor (MBR) implementing a mixed microbial culture predominantly composed of white-rot fungi constitutes the core of the proposed hybrid dye wastewater treatment scheme. The fungi- MBR<sup>78</sup> couples the excellent recalcitrant compound degradability of white-rot fungi with the inherent advantages of an MBR. To sustain an uninterrupted supply of non-specific extra cellular enzyme by fungi, the reactor requires to be operated under a quasi-controlled environment (acidic pH) with simultaneous supply of an easily biodegradable carbon source (e.g., starch used in textile sizing). In case of an integrated textile plant, after the chemical and water recoveries as indicated in figure 2, the concentrates and discarded streams may be fed to the MBR. Depending on the case-specific requirement, the MBR may be augmented by a subsequent advanced oxidation facility (e.g., solar photocatalysis<sup>187</sup>). An internal recycle strategy in between the MBR and the photo reactor may prove to be further beneficial. Depending on the site-specific quality achievement, the final effluent may be reused with or without mixing with fresh water. In case of a plant dealing only with dyeing and finishing, however, a slightly changed approach of water and electrolyte recovery is recommended. In this case since other streams except the

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dyeing and finishing streams are absent, so the concentrated reject-stream generated after water and salt recovery from segregated dye bath effluent and rinse water can not be diluted. Under this condition, the dye bath effluent and rinse water may be directly fed to the MBR-AOP sequence, and then desalinated by membrane (RO/NF), with the concentrate (salt) and permeate (water) being reused.

Due to declining membrane costs<sup>34</sup>, recovery and reuse of chemicals and water using membrane is expected to gain rapid acceptability in near future. The concentrates generated there from and discarded streams (including dye), however, entail further effective economical treatment. This may be realized by an on site membrane separated fungi reactor. Requirement of small plant size is one of the inherent advantages of MBR process. The fungi-MBR<sup>78</sup>, in addition, can achieve excellent effluent quality. Besides, post treatment of the MBR-permeate by an AOP will ensure complete decoloration. Moreover, use of the AOP for post treatment will minimize its light penetration limitation, which would be significant if it were used for pre-treatment. Last but not least, the approach to utilize solar-light for photocatalysis adds to the effort to conserve energy sources. Based on this reasoning, the proposed conceptual integrated treatment scheme appears to be attractive.

This paper intends to underscore the indispensability of hybrid technology for dye wastewater treatment and endorses the inclusion of energy and water reuse plan within the treatment scheme. However, the proposed layout is certainly not claimed to be a panacea for textile dye wastewater. It is rather a demonstration of one of the probable suitable combinations. In line with the broad spectrum of hybrid technologies portrayed in this paper, some additions/modifications to the proposed scheme may also be considered. For instance, simultaneous addition of adsorbent in the MBR<sup>189</sup>, utilization of concurrent AOP-adsorption system<sup>91,132</sup> etc., are worth exploring.

Other approaches may enjoy case-specific superiority over the proposed scheme. For example, with more advancement in the reactor design for AOPs, the partial pre-oxidation by AOP (may be combination among AOPs themselves) prior to MBR treatment may appear to be more appropriate in near future. Conversely, incineration/ wet air oxidation of dye bath concentrate (possessing high calorific value<sup>34</sup>) remaining after material and water recovery by membrane may also furnish an attractive solution.

## VII.CONCLUSION

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Residual dyes along with other auxiliary chemical reagents used for processing, impurities from the raw materials and other hazardous materials applied in the finishing process impose massive load on wastewater treatment system. This eventually leads to a poor color and COD removal performance. The release of colored wastewater in the ecosystem is a remarkable source of esthetic pollution, eutrophication and perturbations in aquatic life. These concerns have led to new and/or stricter regulations concerning colored wastewater discharges, rendering the decolorization process further difficult and costly. To combat this problem, researchers have put forward a wide variety of hybrid decolorization techniques. Based on the array of potential hybrid technologies and the available cost information, it can be concluded that hybrid technologies having biological processes as the core appear to be the most prospective ones. It should also be emphasized here that inclusion of energy and water reuse plan within the treatment scheme is an imperative. In this context membrane technology has an immense role to play. Membrane bioreactor implementing special dye-degrading microorganism and involving simultaneous addition of adsorbent in MBR may surface as a potential contender among present-day dye wastewater treatment processes. The MBR technology may as well be combined with advanced oxidation facilities. Case-specific selection of the appropriate hybrid technology is the key to realization of a feasible system.

## Hybrid Treatment Systems for Dye Wastewater

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# Hybrid Treatment Systems for Dye Wastewater

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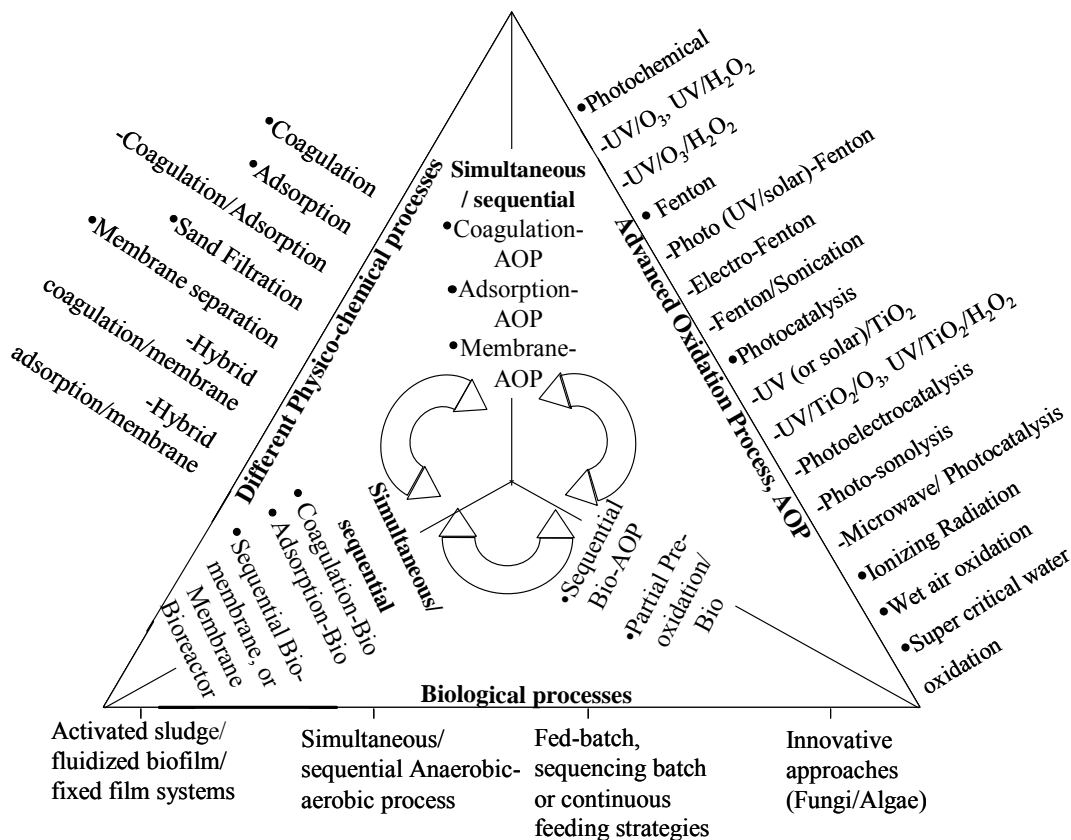


Figure 1: Simplified representation of broad spectrum of combinations proposed in the literature

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**Table: 1 Advantages and shortcomings of individual dye wastewater treatment techniques**

Process	Advantages	Disadvantages	Selected Ref.
Biological	Cost-competitive option. Direct, disperse and basic dyes have high level of adsorption on to activated sludge.	Dyes are generally toxic and very resistant to biodegradation. Acid and reactive dyes are highly water-soluble and have poor adsorption on to sludge.	160
Coagulation	Economically feasible; satisfactory removal of disperse, sulphur and vat dyes.	Removal is pH dependent; produces large quantity of sludge. May not remove highly soluble dyes; unsatisfactory result with azo, reactive, acid and basic dyes.	61,79,179
Activated C adsorption	Good removal of wide variety of dyes, namely, azo, reactive and acid dyes; especially suitable for basic dye.	Removal is pH dependent; unsatisfactory result for disperse, sulfur and vat dyes. Regeneration is expensive and involves adsorbent loss; necessitates costly disposal.	61,79,179
Ion exchange	Adsorbent can be regenerated without loss, dye recovery conceptually possible.	Ion exchange resins are dye-specific; regeneration is expensive; large-scale dye recovery cost-prohibitive.	179,196
Membrane filtration	Appropriate membrane may remove all types of dyes and thus realize reusable water from dye-bath effluent.	Concentrated sludge production and costly membrane replacement impede widespread use.	36
Chemical oxidation	Initiates and accelerates azo-bond cleavage.	Thermodynamic and kinetic limitations along with secondary pollution are associated with different oxidants. Not applicable for disperse dyes. Negligible mineralization possible, release of aromatic amines and additional contamination with chlorine (in case of NaOCl) is suspected.	179,196
Advanced oxidation processes, AOPs	Generate a large number of highly reactive free radicals and by far surpass the conventional oxidants in decolorization.	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 <sub>3</sub>	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.	61,73,79, 90,140, 179
UV/H <sub>2</sub> O <sub>2</sub>	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.	73,140
Fenton's reagent	Effective decolorization 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	79,140, 179, 203
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)	105
Electrochemical	Effective decolorization of soluble/insoluble dyes; reduction of COD possible. Not affected by presence of salt in wastewater.	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.	40,179

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Sonolysis	Addition of chemical additives not required and hence does not produce excess sludge.	Requires a lot of dissolved gas (O <sub>2</sub> ); complete decoloration and mineralization by sonification alone are not economical at present level of reactor development.	2,11
Ionizing Radiation	No sludge production; effective oxidation at lab scale.	Requires a lot of dissolved O <sub>2</sub> ; complete decoloration and mineralization by stand alone application not possible. Energy efficient scale-up yet to be achieved.	179
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.	10,11

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**Table 2. List of typical examples of combinations among AOPs for dye wastewater treatment**

Different dye chromophores: <sup>N=N</sup>: Azo, <sup>AQ</sup>: Anthraquinone, <sup>TPM</sup>: Triphenylmethane dye, <sup>TH</sup>: Thiazine; <sup>XN</sup>: Xanthene; <sup>C=C</sup>: Stilbene dye; <sup>TC</sup>: Phthalocyanine

Technology	Dye/ Wastewater	Details	Ref. (Year)
UV/ O <sub>3</sub>	2-naphthalenesulfonate [Azo Dye intermediate]	Mineralization of 2-NS via ozonation (40 mg/l) is remarkably enhanced by UV radiation (60.35 W/m <sup>2</sup> , 254 nm), tripling the rate. Not much difference in 2-NS decomposition.	39 (2002)
UV/O <sub>3</sub> , UV/H <sub>2</sub> O <sub>2</sub>	Acid <sup>N=N</sup> - red 1/ black 1/ red14/ red 18/ orange 10/ yellow 17/ yellow 23; Direct <sup>N=N</sup> yellow 4	Decoloration (20 mg/l dye): 100% in 10 min. by O <sub>3</sub> (6 l/min. O <sub>2</sub> ) with/without UV; 80% in 25 min. by H <sub>2</sub> O <sub>2</sub> -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.	192 (1995)
UV/H <sub>2</sub> O <sub>2</sub>	Hispamin Black CA [Direct <sup>N=N</sup> Black 22]	UV (125 W)- H <sub>2</sub> O <sub>2</sub> (565.8 mg/l, 16.6 mM): Complete decoloration (35 min.) & 82% TOC removal (60 min.) for 40 mg/l dye at natural pH (7.5), although subsequent toxicity test recommended.	46 (2002)
UV/H <sub>2</sub> O <sub>2</sub>	Acid dye [orange 8 <sup>N=N</sup> / blue 74 <sup>C=C</sup> , Methyl orange <sup>N=N</sup> ]	Removal by Only UV (15W, 253.7 nm, incident photon flux = 6.1x10 <sup>6</sup> Einstein s <sup>-1</sup> , 4.54≤pH≤5.5) and only H <sub>2</sub> O <sub>2</sub> in absence of UV was negligible. <b>Combined:</b> Decolorization rate rises by increasing the initial dosage of H <sub>2</sub> O <sub>2</sub> up to a critical value ([H <sub>2</sub> O <sub>2</sub> ]/[dye]=50-70) beyond which it is inhibited.	4 (2003)
UV/H <sub>2</sub> O <sub>2</sub>	Reactive- red 120 <sup>N=N</sup> / black5 <sup>N=N</sup> / yellow 84 <sup>N=N</sup>	UV (15 W)/ H <sub>2</sub> O <sub>2</sub> (optimum dose 24.5 mmol/l): <u>15 min.</u> : [Decolorization>65%, COD removal= 40-70%], <u>60 min.</u> : [Decolorization> 99%]; Degradation by products unobjectionable.	152 (2002)
UV/H <sub>2</sub> O <sub>2</sub> and solar/H <sub>2</sub> O <sub>2</sub>	Chlorotriazine Reactive <sup>N=N</sup> Orange 4	Dye removal (0.5 mmol/l), 150 min., pH 3: UV (64W, 365nm)-H <sub>2</sub> O <sub>2</sub> (10 mmol)= 88.68% decolourisation , 59.85% degradation. Sunlight-H <sub>2</sub> O <sub>2</sub> = 80.15% decolourisation, 50.91% degradation. Dye auxiliaries like Na <sub>2</sub> CO <sub>3</sub> , NaOH seriously retard decoloration rate while NaCl does not.	149 (2004)
O <sub>3</sub> followed by UV/ H <sub>2</sub> O <sub>2</sub>	Wastewater from cotton & polyester fiber dyeing textile mill	Under natural pH (10.66) 5 min pre-ozonation (293 mg/l), removing high UV-absorbing components (60% reduction in UV <sub>254</sub> ), accelerated subsequent 55 min. H <sub>2</sub> O <sub>2</sub> (50 mmol/l)-UV(25W) treatment, enhancing its COD & TOC removal efficiency by a factor of 13 & 4, respectively; the combined treatment yielding 25% COD, 50% TOC & complete color removal (Initial COD=1476 mg/l; TOC= 336mg/l).	8 (2001)
UV /H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub>	Wastewater containing disperse dyestuff & pigments	99% COD (Initially 930 mg/l) and 96% color removal in 90 min. [pH=3; H <sub>2</sub> O <sub>2</sub> =200 mg/l; O <sub>3</sub> = 2 g/h; 15 W lamp, 254 nm]. Over 90% removal by UV/O <sub>3</sub> with less cost due to no requirement of pH adjustment and H <sub>2</sub> O <sub>2</sub> .	12 (2004)
Fe <sup>+2</sup> /O <sub>3</sub>	Simulated disperse dye bath ( CI disperse- violet 931, blue 291; two more azo dyes and compounds)	95% color (Dyes= 0.5 g/l), 48% COD (initially= 3784 mg/l) removal and 10 times improvement in BOD <sub>5</sub> /COD ratio at natural acidic pH of dye bath ( 3.6 mM Fe <sup>+2</sup> ; [Fe <sup>+2</sup> ]: [O <sub>3</sub> ]= 1:14; FeSO <sub>4</sub> .7H <sub>2</sub> O= 1000 mg/l). Negligible TOC removal is due to low O <sub>3</sub> dose of 14 g/l.	9 (2001)
UV/Fenton	Disperse <sup>N=N</sup> red 354	85% color removal (Dye=100 mg/l) & 90% COD removal within 10 mins. with 24.5 mmol H <sub>2</sub> O <sub>2</sub> /l and 1.225 mmol FeSO <sub>4</sub> /l at pH=3, resulting effluent having only 7.29% inhibition in bioluminescence test. Presence of dispersing agent reduces removal efficiency.	153 (2003)
UV/Fenton	Reactive <sup>N=N</sup> brilliant red X-3B	Stable decoloration (Dye= 7.7x10 <sup>-3</sup> M) within 20 min. with [H <sub>2</sub> O <sub>2</sub> ]= 18x10 <sup>-4</sup> M, [Fe <sup>+2</sup> ] or [Fe <sup>+3</sup> ]=1.1x10 <sup>-4</sup> M, 75W UV (λ<320nm) lamp. Use of Fe <sup>+2</sup> is preferable to Fe <sup>+3</sup> because of faster reaction rate with H <sub>2</sub> O <sub>2</sub> and evolution of HO.	226 (2001)
Solar/Fenton	Orange II (Acid <sup>N=N</sup> orange 7)	Decoloration of highly concentrated (2.9 mM ≡ 0.8g/l) dye in less than 2 hr and 95% mineralization within 8hr by a solar simulator (90 mW cm <sup>-2</sup> ) and also by natural sunlight (80 mW cm <sup>-2</sup> ) with 0.92 mM Fe <sup>+3</sup> and 10 mM H <sub>2</sub> O <sub>2</sub> /hr [pH=2].	20 (1996)
Solar/Fenton	Monoreactive <sup>N=N</sup> Procion red H-E7B, Hetero-bireactive <sup>N=N</sup> Red cibacron FN-R, Standard trichromatic mixture	Sunlight, supplying higher number of photons (3-4x10 <sup>3</sup> W cm <sup>-2</sup> ) than the low power artificial source (350 nm, 6W, 1.3x10 <sup>-4</sup> W cm <sup>-2</sup> ), resulted in faster complete decoloration (15-30 min.) and complete (or near) TOC removal (20-60 min.) for dye concentration of 100 mg/l with 10 mg/l Fe <sup>+2</sup> and 100-250 mg/l H <sub>2</sub> O <sub>2</sub> [pH=3].	207 (2004)
Cu(II)/Glucaric acid/H <sub>2</sub> O <sub>2</sub>	Direct Chicago sky blue <sup>N=N</sup> , Methyl or	Over 90% decolorization of 100 ppm dye within 24 hr. (70-80% within first 6 hr.) with 10 mM CuSO <sub>4</sub> , 200 mM	212

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	ange <sup>N=N</sup> , Reactive <sup>N=N</sup> black 5; Poly <sup>AQ</sup> B-411, Reactive <sup>AQ</sup> blue 2, RBBR <sup>AQ</sup> , Acridin (Basic) <sup>AQ</sup> orange; Azure blue <sup>TH</sup> , Crystal violet <sup>TPM</sup>	H <sub>2</sub> O <sub>2</sub> and low dose of glucuric acid (15 mM). Insensitive to pH, unlike fenton reaction.	(2004)
UV/ O <sub>3</sub> /TiO <sub>2</sub>	Textile effluent containing Reactive <sup>N=N</sup> dye	Removals (60 min.)- <b>Photocatalysis</b> (0.1 g/l anatase TiO <sub>2</sub> , 125 W, fluency rate 31.1 J m <sup>-2</sup> s <sup>-1</sup> , pH=11): Color= 90%, TOC= 50%; <b>Ozonation</b> (pH=11, 14 mg/l): Color= 60%, TOC= negligible; <b>Combined</b> : Color=100%, TOC> 60%, Toxicity=50%	146 (2000)
UV/ H <sub>2</sub> O <sub>2</sub> /TiO <sub>2</sub>	Eosin Y <sup>XN</sup>	Enhanced decoloration (100% for 50 mg/l dye) & mineralization (95%) in 1 hr (19W lamp, 1g/l TiO <sub>2</sub> , 100 mg/l H <sub>2</sub> O <sub>2</sub> , pH=5.4) along with 85% reduction in toxicity.	173 (2003)
Solar/ H <sub>2</sub> O <sub>2</sub> / Polymeric metalloporphyrins	Acridin (Basic) <sup>AQ</sup> orange	% [Decoloration, Degradation]: <u>Hg lamp</u> (450 W, 8hr) Catalysis (3mg/35ml) with H <sub>2</sub> O <sub>2</sub> (0.4 g/l) = [87, 92]; without H <sub>2</sub> O <sub>2</sub> =[77, 86]. <u>Solar light</u> ( 3hr) Catalysis without H <sub>2</sub> O <sub>2</sub> = [77, 90]. Dye= 13.3 mg/l, high pH favourable.	38 (2002)
Pulsed streamer corona discharge (electrical)/ H <sub>2</sub> O <sub>2</sub>	Rhodamine B <sup>XN</sup> (Basic), Acid <sup>N=N</sup> Methyl orange, Direct <sup>N=N</sup> Chicago sky blue	Pulsed high voltage (20 kV, 25Hz) electrical discharge in water, yielding photo-dissociation of added H <sub>2</sub> O <sub>2</sub> (8.8x10 <sup>-4</sup> mol/l), showed enhanced decoloration rate (100% for 10 mg/l dye in 60 min.) as compared to individual process-performances.	200 (2002)
<b>Photoelectrochemical</b>	Methylene blue <sup>TH</sup>	Chemical synergism of photochemical & electrochemical processes yielded enhanced decoloration (95%), COD removal (87%) & TOC removal (81%) in 30 min [Dye=1 mmol/l; 500W lamp, 6.64 mWcm <sup>-2</sup> , 1gTiO <sub>2</sub> /200 ml; 30 V DC; Natural pH(6.6)].	6 (2002)
Microwave (MW)/ Photocatalysis	Rhodamine B <sup>XN</sup> (Basic)	In contrast to negligible removal by MW (300W), or less removal by photocatalysis (75W, 0.3mW cm <sup>-2</sup> ; 30 mg TiO <sub>2</sub> /30 ml) alone, combined process achieved 97% decoloration (Dye= 0.05 mM) and 73% TOC removal within 3 hrs at pH=5.5.	84 (2002)
Photoelectrocatalysis	Reactive <sup>N=N</sup> brilliant orange K-R	<b>Decoloration</b> and <b>TOC</b> removal of dye (0.5 mM) in 0.5 mmol l <sup>-1</sup> NaCl solution within 60 min. (Natural pH) : i) Adsorption on packed material: <b>9%</b> , -- ; ii) Photocatalysis [TiO <sub>2</sub> (antase= 70%) coated quartz sand, 500 W high-pressure mercury lamp]: <b>70%</b> , <b>20%</b> ; iii) Electro-oxidation [30.0 V DC cell voltage, reaction flow rate=190 ml min <sup>-1</sup> , 0.05 MPa airflow]: <b>77%</b> , <b>7%</b> ; iv) Photoelectrocatalysis: <b>96%</b> , <b>38%</b> . Obvious enhancement effect (unlike photocatalysis) of salt in solution.	238 (2003)
UV/Electro-Fenton	Reactive <sup>N=N</sup> Red 120	<b>TOC removal [180 min.]</b> : 30%; <b>Decoloration [30 min.]</b> : 75-85% for 60-100 mg/L concentration; Low efficiency due to radical scavenging by the graphite cathode. <b>Detoxification [90 min.]</b> : Safely disposable.	116 (2004)
Gamma irradiation/ H <sub>2</sub> O <sub>2</sub>	Reactive <sup>TC</sup> blue 15 (Chrozol turquoise blue G), Reactive <sup>N=N</sup> black 5 (Chrozol black 5)	H <sub>2</sub> O <sub>2</sub> , yielding .OH by reacting with hydrated electron formed in radiolysis of water, achieved enhanced decoloration (100%, 50 ppm dye) and COD removal (76-80%) with 1 and 15 kGy doses for RB5 and RB15, respectively, decoloration (%) being the highest at the lowest dose rate (0.14 kGy/h).	194 (2002)
Sonolysis/ MnO <sub>2</sub>	Acid <sup>N=N</sup> red B	Sonication (50 kHz, 150 W) enhanced oxidation property of MnO <sub>2</sub> (1 g/l) by improving mass transfer, removal of passivating outer oxide layer & production of H <sub>2</sub> O <sub>2</sub> , eventually realizing 94.93% decolorization (argon atmosphere) and 48.12 % TOC removal (oxygen atmosphere) [initial pH=3, 240 min.].	68 (2003)
Sonolysis / Fenton's reaction	Acid <sup>N=N</sup> Methyl orange	Addition of FeSO <sub>4</sub> ([Fe <sup>+2</sup> ]= 0.1-0.5 mM) resulted in Fenton's reaction with H <sub>2</sub> O <sub>2</sub> evolving from simultaneous sonification (500 kHz, 50W) and achieved 3-fold increase in decoloration (15 min., 10μM dye) and TOC removal (50%, 20 min.) as compared to sonification only.	93 (2000)
Sonolysis/O <sub>3</sub>	C.I Reactive <sup>N=N</sup> black 5 (RBB)	Combined sonolysis (520 kHz) and ozonation (irradiation intensity, O <sub>3</sub> input and volume were 1.63 W cm <sup>-2</sup> ; 50 l h <sup>-1</sup> ; and 600 ml) showed synergistic effect, doubling the decolorization (100%, 15 min.) and mineralization (76%, 1hr) rate.	90 (2001)
Sonolysis/O <sub>3</sub>	Acid <sup>N=N</sup> 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 (10μM dye) and 80% mineralization (3 hr) as compared to 20-30% by stand-alone application.	53 (2000)
Sonolysis/UV /O <sub>3</sub>	C.I Acid <sup>N=N</sup> orange 7	Enhanced O <sub>3</sub> (40 g/m <sup>3</sup> ) diffusion by mechanical effects of ultrasound (520 kHz, 600 W) & the photolysis (108W) of ultrasound-generated H <sub>2</sub> O <sub>2</sub> to produce .OH led to complete decoloration (Dye= 57μM), 40% TOC removal & an im-	206 (2004)

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Sonolysis /H <sub>2</sub> O <sub>2</sub>	Vinylsulphone reactive dyes [C.I Reactive- Yellow 15 <sup>N=N</sup> , Red 22 <sup>N=N</sup> , Blue 28, Blue 220, Black 5 <sup>N=N</sup> ; Remazol dark black N 150%]	provement of BOD <sub>5</sub> /TOC from zero to 0.45 within 60 min (initial pH=5.5). Combined sonolysis (20 kHz) and H <sub>2</sub> O <sub>2</sub> (3.49 mol/l) showed synergistic effect, doubling the decolorization (90-99% depending on dye, 4 hr.) rate.	216 (2003)
Sonolysis/UV/H <sub>2</sub> O <sub>2</sub>	Cuprophenyle yellow RL <sup>C=C</sup> (Acid!)	Sonication (320 kHz) dramatically enhanced oxidation efficiency of UV(6@11W)+H <sub>2</sub> O <sub>2</sub> ( 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 1 <sup>st</sup> order kinetics.	63 (1999)
Sonolysis /UV/TiO <sub>2</sub>	Naphthol blue back <sup>N=N</sup>	Simultaneous or sequential sonolysis (640 kHz, 240 W) and photocatalysis (1g/L TiO <sub>2</sub> ) showed additive effect on decoloration (100% in 200 min.; 50μM dye) while, in terms of mineralization, simultaneous application (50%, 4hr; 80%, 12 hr), due to mass transfer improvement of reactants & products to and from TiO <sub>2</sub> surface, performed better than sequential application (<20%, 4hr; 50%, 12hr).	198 (2000)
Sonolysis/UV/TiO <sub>2</sub>	Acid <sup>N=N</sup> - red 1, Orange 8	Simultaneous sonolysis (20 kHz, 15 W) and photocatalysis (0.1g/L TiO <sub>2</sub> ) showed synergistic effect on decoloration/ degradation (2.5 x10 <sup>-5</sup> M dye) due to promoting de-aggregation of TiO <sub>2</sub> , desorption of reactants & products from TiO <sub>2</sub> surface & mainly by scission of produced H <sub>2</sub> O <sub>2</sub> , thereby, increasing oxidizing species in aqueous phase.	148 (2003)
Sonolysis UV/ H <sub>2</sub> O <sub>2</sub>	C.I reactive <sup>N=N</sup> red 120	Sonification (320 kHz) significantly enhanced the decoloration (Dye= 0.1 g/L) efficiency of UV/ H <sub>2</sub> O <sub>2</sub> . Higher flow rate (insufficient irradiation) necessitated higher dosing rate of H <sub>2</sub> O <sub>2</sub> .	64 (2001)
Sonoelctrolysis	Acid <sup>N=N</sup> Sandolan Yellow	Electro-oxidation of dye (50 mg/L) in saline solution (0.01 mol/L NaCl) involving insitu generation of hypochlorite ion was enhanced using ultrasound (20 kHz, 22 W) when carried out in a semi-sealed cell, which minimized the effects of ultrasonic degassing.	135 (2000)

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**Table 3. List of typical examples of combinations between conventional physico-chemical processes and AOPs****Different dye chromophores:** <sup>N=N</sup>: Azo, <sup>AQ</sup>: Anthraquinone, <sup>TC</sup>: Phthalocyanine

Technology	Dye/ Wastewater	Details	Ref. (Year)
Fenton/ Chemical coagulation	C.I direct <sup>N=N</sup> blue 202, C.I reactive <sup>N=N</sup> black 5; PVA	81-86% COD (Initially > 1000 mg/l) removal & decoloration (Dye= 200 mg/l) in 2 hrs. with [H <sub>2</sub> O <sub>2</sub> ]/[FeSO <sub>4</sub> ]= 1000/400 at pH=3, while subsequent coagulation at pH=7-10 with 100 mg/l PAC & 2mg/l polymer reduced floc settling time, enhanced decoloration and reduced soluble Fe in effluent.	131 (1997)
Fenton+ Chemical coagulation	Disperse- Blue <sup>N=N</sup> 106, Yellow <sup>AQ</sup> 54; Reactive- Blue <sup>AQ</sup> 49, Yellow <sup>N=N</sup> 84	<b>Coagulation (pH= 5-7):</b> Removal per mol Fe <sup>+3</sup> [COD, DYE]: Disperse (0.74-0.93mM FeCl <sub>3</sub> ) =[460.2-477g, 525.7-672.7]; Reactive (1.85-2.78 mM FeCl <sub>3</sub> ) =[37.4-86.5g, 109.5-192.7g]. <b>Fenton (pH= 3; 30 min; [Fe<sup>+2</sup>]: [H<sub>2</sub>O<sub>2</sub>]=1:0.2-1:0.37):</b> Removal per mol Fe <sup>+2</sup> [COD, DYE]: Disperse=[14-80g, 3.7-20.8g]; Reactive=[114.2-199.6g, 118.9-489.2g]. <b>Combined:</b> Both dyes, 90%COD & 99% dye removal.	101 (2004)
O <sub>3</sub> / Coagulation	Azo dye manufacturing wastewater (subjected to chlorination)	REMOVAL: After <b>Ozonation</b> [70 min.; 56 mg O <sub>3</sub> /min.; 1.6 l/min.; pH= 10.3] COD= 25%, Color= 43%.. After subsequent <b>Ca(OH)<sub>2</sub> coagulation</b> [787 mg/l, pH= 12] COD= 50%, TOC= 42%, Color= 62%; effective removal of chloroorganics after two stages.	186 (1998)
Coagulation/ O <sub>3</sub>	Textile wastewater	Coagulation [Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , 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.	209 (1994)
Multistage (Coagulation/ O <sub>3</sub> )	Dye manufacturing wastewater	Single stage coagulation (2.5%, v/v, FeCl <sub>2</sub> ; 35 mg/l polymer; pH=8.5) followed by ozonation (pH=11; <b>90 min.</b> ) achieved [19% COD, 88% color] and [67% COD, 99.3% color] removal, respectively (initial COD=7700mg/l; Color=67000 ADMI). Three times repetition of the sequence while keeping total ozonation time same (3@30 min.) achieved >90% COD & 99.99% color removal, the superiority of multistage treatment being less convincing for wastewater with simpler composition.	86 (1998)
Coagulation/ UV-Fenton	Integrated plant containing variety of processes ranging from desizing to dyeing and ultimate finishing	UV (20W)/TiO <sub>2</sub> (1 g/L)/ H <sub>2</sub> O <sub>2</sub> (10mM)/Fe <sup>+2</sup> (1mM) treatment (pH=4) following coagulation treatment achieved complete decoloration (30 min.) & a maximal 48% (over that achieved by coagulation) COD removal (1 hr.), the COD of raw, coagulated and oxidized sample being 1063, 556 & 269 mg/L, respectively.	18 (2003)
Coagulation / Carbon adsorption	C.I reactive <sup>N=N</sup> red 45, C.I reactive <sup>N=N</sup> green 8	Removal (Dye= 1g/l): <b>After AlCl<sub>3</sub>.6H<sub>2</sub>O coagulation</b> [0.8 g/l; pH= 3.5]: RR 45 [ Color 98.8%, TOC 98.1%, COD 93.4%]; RG 8 [Color 99%, TOC 96.9%, COD 83.8%]. <b>After carbon adsorption</b> [0.24 & 0.84 g/l; 2 hr]: RR 45 [Color 99.9%, TOC 99.7%, COD 95.7%]; RG 8[Color 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.	163 (2004)
Photocatalysis/Adsorption (Powdered activated carbon, PAC)	Humic acid (Natural coloring matter)	3-4 hrs irradiation induced decrease in UV280, UV254, TOC and COD and simultaneous improvement of biodegradability with no significant decrease in adsorptivity of subsequent PAC.	22 (1996)
Solvent extraction (& dye recovery) / Fenton's reagent	1-diazo-2-naphthol-4-sulfonic acid (acid dye intermediate)	82% extraction using solvent (trialkylamine N <sub>235</sub> ) and subsequent dye recovery by stripping led to 95% decoloration of the original effluent. Subsequent raffinate treatment (after lime neutralization) by Fenton's reagent achieved achromatic effluent with COD < 100 mg/L.	87 (2004)
O <sub>3</sub> /Ion exchange	Cu-complex Direct <sup>N=N</sup> Blue 80	Concurrent decoloration & metal release by 0.2 mg O <sub>3</sub> /mg dye and subsequent metal removal by strong acid cation-exchange resin at pH=2 achieved Cu-concentration below detectable limits in the effluent.	97 (1996)
Adsorption (Fluidized GAC) +O <sub>3</sub>	Acid blue 9, Mordant <sup>N=N</sup> black 11, Reactive <sup>AQ</sup> blue 19, Reactive <sup>N=N</sup> orange 16	Influent: pH=5.1-9.2, COD=250-1800 mg/l, SS= 45-320 mg/l, turbidity (NTU)=50 -210. Combined ozonation and GAC adsorption (4l O <sub>3</sub> /min per 100 gm GAC) offers mutual enhancement namely regeneration of GAC & catalysis of O <sub>3</sub> .	132 (2000)
Adsorption (GAC) +UV/ H <sub>2</sub> O <sub>2</sub>	Reactive Everzol Black-GSP	Simultaneous adsorption (8g/L) & UV- H <sub>2</sub> O <sub>2</sub> 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.	91 (2002)
Adsorption (β-FeOOH)/ oxidative	C.I. Reactive <sup>N=N</sup> Red 198	Adsorption onto granulated β-FeOOH (170mg/g) and its repeated reuse (6 cycles) following regeneration by catalytic	107

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(H <sub>2</sub> O <sub>2</sub> ) regeneration		oxidation using H <sub>2</sub> O <sub>2</sub> (7mg dye/mg; 6hr@24.5 ml/min.); selective adsorption/oxidation, lower oxidant dose and no conventional concentrate treatment. Simultaneous treatment recommended for high salt containing w.water.	(2002)
Ion-exchanger (Quarternized ammonium cellulose) / Chemical reduction (Bisulfite-mediated borohydride)	Orange II (Acid <sup>N=N</sup> Orange 7), Reactive <sup>N=N</sup> red 180	Anion exchanger bound 383mg/g of Orange II & 272 mg/g of reactive dye while subsequent KBH <sub>4</sub> /NaHSO <sub>3</sub> (2mM/10mM) reduction of dye (1mM 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.	117 (1997)
Adsorption (PAC)/ Wet air oxidation (WAO)	Chemictive Brill. Blue R (Reactive <sup>AQ</sup> ); Cibacorn Turquoise Blue G (Reactive <sup>TC</sup> )	Efficient treatment of lower concentrations of unhydrolyzed 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 <sub>2</sub> partial pressure 0.69-1.38 Mpa), and recycling the regenerated carbon.	191 (2002)
Adsorption(CuFe <sub>2</sub> O <sub>4</sub> )/ Catalytic combustion	Acid <sup>N=N</sup> Red B	Dye, pre-concentrated on adsorbent/catalyst CuFe <sub>2</sub> O <sub>4</sub> (>95% removal from 100mg/l; pH<5.5, dose= 0.1g/50ml), 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 <sub>2</sub> O <sub>4</sub> was regenerated allowing efficient reuse over extended cycles.	223 (2004)
Adsorption (ferrous modified GAC)+ Microwave (MW) induced Oxidation	Argazol Blue BF-BR 150% (Bi-functional <sup>N=N</sup> reactive dye)	98.3% decoloration and 96.8% COD removal was achieved when dye solution (50ml, 300mg/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 <sup>+2</sup> from GAC surface under reuse for many times.	166 (2004)
Adsorption (GAC)/ Microwave (MW) regeneration	C.I Acid <sup>N=N</sup> 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.	176 (2004)
Sonication/ Fe <sup>0</sup> reduction	C.I Acid <sup>N=N</sup> Orange 7	Pulsed sonication (20 kHz, 250W), by improving mass transfer & also increasing active sites on Fe-surface, dramatically enhanced dye (50 mg/L) decoloration efficiency of mild reducing agent Fe <sup>0</sup> (1 g/l, pH=3), the combined process achieving 91% dye removal in 30 min. following 1 <sup>st</sup> order kinetics.	237 (2005)
Membrane-based ozonator	Blue 19 reactive dye; Untreated exhausted dye-bath	Thin coating of TiO <sub>2</sub> & γ-Al <sub>2</sub> O <sub>3</sub> on ceramic membrane (ZrO <sub>2</sub> , α-Al <sub>2</sub> O <sub>3</sub> ) 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 hrs.	45 (2003)
Photocatalytic membrane reactor	Congo red <sup>N=N</sup> , Patent blue <sup>N=N</sup>	The continuous photocatalytic membrane (NF; 30-70 L/m <sup>2</sup> h) reactor with suspended TiO <sub>2</sub> (1g/l) & immersed UV lamp (125W) outperformed its counterpart with TiO <sub>2</sub> entrapped on membrane and irradiated with external lamp (500W), achieving almost complete photodegradation of dyes (500 mg/l) with higher rate.	145 (2004)
Membrane/ Wet air oxidation,WAO	Disperse <sup>N=N</sup> blue CI 79	NF membrane achieved >99% color and 97% COD rejection of dye compound while the homogeneous copper sulfate catalyzed WAO (160°-225°C, O <sub>2</sub> partial pressure 0.69-1.38 Mpa) reduced 90% COD from concentrate (120 min.).	55 (2000)
Membrane/ Wet air oxidation,WAO	Dyeing wastewater containing Reactive blue, Indigo, Sulphur black & other process chemicals	Replacing O <sub>2</sub> with stronger oxidant H <sub>2</sub> O <sub>2</sub> (50% of stoichiometric amount) & adding Cu-AC catalyst (2g/l), 80% TOC & 90% color was removed from membrane-concentrate by WO under mild condition (110°C ,Total P= 50 kPa) in 30 min.	118 (1998)
Membrane/ Sonication/ WAO	Reactive <sup>TC</sup> Turquoise blue CI25	NF membrane (1.5 Mpa; flux=0.084m/h) removed 90.3% COD & 98.7% color from <i>pure dye solution</i> (COD=1500 mg/l), while WO (190°C, O <sub>2</sub> 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 <i>actual wastewater</i> to be amenable to subsequent WO.	54 (1999)
Membrane/ O <sub>3</sub>	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 color & Cu, and only 15% of salt removal while subsequent ozonation (7.73 mg/l.min, pH=11) removed color from the concentrate following 1 <sup>st</sup> order kinetics, the rate decreasing with increasing initial dye color.	222 (1998)
UV-Fenton/ Coagulation/Membrane	Reactive <sup>N=N</sup> (Procion Red HE7B)	Complete color removal (Dye= 50 mg/l) and 79% TOC removal within 20 min. by photo-fenton (PH=3; [H <sub>2</sub> O <sub>2</sub> ]/[Fe <sup>+2</sup> ]= 20:1; 4@ 15W UV lamp). However 9 times increase in dissolved solids warrants subsequent coagulation/membrane system for reuse in dye/rinse process.	88 (1999)
Physico-chemical / Membrane (UF/ NF)	Synthetic textile manufacturing wastewater	<b>Raw water:</b> 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. <b>Physico-</b>	25 (2002)

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**chemical** (pH = 8.5,  $C_{DK-FER20}$  = 200 mg/L,  $C_{nalco,flocculant}$  = 1 mg/L): 50% COD removal; **NF membrane** (flow rate =400 L/h, TMP=1 MPa): 100% COD removal, 85% conductivity retention.[Reusable]

Physico-chemical / Membrane (NF)	Textile wastewater	<b>Raw water:</b> Conductivity (mS/cm) 4.53; COD (mg/L) 1630. <b>Physico-chemical</b> (pH = 12, $Fe^{+2}$ = 700 mg/L): 72.5% COD removal; <b>NF membrane</b> (flow rate =200 L/h, TMP=20 bar, flux= 8-10 L/m <sup>2</sup> h): COD<100mg/l; Conductivity <1 mS/cm	26 (2003)
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.	139 (2002)
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.	219 (1996)
Membrane (UF)/ Adsorption (Activated Carbon cloth, ACC)	Acid <sup>N=N</sup> Orange II, Acid <sup>N=N</sup> 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 (38-180mg/g, dye-specific). Replacing UF with NF, or UF membrane wrapped up in a pleated ACC recommended to avoid early breakthrough of ACC.	168 (2000)

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**Table 4. List of typical examples of combinations between biological treatment and other technologies**

**Different dye chromophores:** <sup>N=N:</sup> Azo, <sup>C=C:</sup> Stilbene.

Technology	Dye / Wastewater	Details	Ref. (Year)
Chemical (NaOCl)/ Bio (Anaerobic)	Kraft E1 effluent (containing lignin and other colored compounds like quinones, chalcones, stilbenes)	NaOCl (0.1 kg Cl/kg color; pH=10) achieved 90% color removal with 50% increase in low molecular mass AOX which was amenable to subsequent anaerobic treatment, although a simultaneous small amount of color reversion occurred during anaerobic stage. A short term solution for combined decoloration & dechlorination.	47 (1994)
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 kgCODMn/kgVSS.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 kgCODMn/kgVSS.day) process achieved similar removal, but with 20% more excess sludge due to more dissolved (in addition to suspended) substance removal during coagulation.	229 (1996)
Coagulation (Na-bentonite)/ Activated sludge	Wastewater from plants dyeing & finishing natural/ synthetic fibers	Chemical pretreatment (2g/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 decoloration, only 20% residual soluble COD removal.	57 (2002)
Fluidized biofilm/ coagulation/ electrochemical oxidation	Synthetic textile dyeing wastewater	Biofilm of specially isolated microbes on support media achieved 68.8% COD <sub>cr</sub> (initial= 800-1000 mg/l) and 54.5% color removal while those achieved by overall combined system (FeCl <sub>3</sub> .6H <sub>2</sub> O dose of 3.25x10 <sup>-3</sup> mol/l; Electrooxidation: 2.1 mA/cm <sup>2</sup> of current density and 0.7 l/ min flow rate) were 95.4% and 98.5%, respectively.	100 (2002)
Fenton or Powdered activated C (PAC)/Fixed bed biofilm/ Fenton	Disperse dyestuff wastewater	Enhanced removal by previously acclimatized biomass on fixed bed due to increased biodegradability (BOD <sub>5</sub> :COD from 0.06 to 0.432) by fenton (H <sub>2</sub> O <sub>2</sub> : FeSO <sub>4</sub> .7H <sub>2</sub> O = 700:3500, mg/l) or PAC pretreatment. COD removal (initially 17200 mg/l) <i>separately</i> at pretreatment, biological & post treatment were 50%, 85% & 85%, respectively.	3 (1999)
Coagulation/ Electrochemical oxidation/ Activated sludge	15 dyes used in a plant making primarily cotton and polyester fibers and small quantity of wool	Influent: COD=800-1600 mg/l, Transparency <4cm, Conductivity= 2000 μmho/cm, pH= 6-9. COD concentration (100 mg/l) and transparency (30) amply satisfies the government safe discharge standard by employing Poly aluminium chloride (40 mg/l, with polymer concentration 0.5mg/l), electrochemical oxidation (pH≈7, current density= 53.4 mA/cm <sup>2</sup> , 1 l/ min of flow rate) and the subsequent activated sludge process.	129 (1996)
Bio/ Electroflocculation/ Flotation/ Filtration	Wastewater from plants dyeing & finishing natural/ synthetic fibers	Although electroflocculation is effective without biological pretreatment, the same enhanced its performance, while subsequent flotation and bentonite filtration completed sludge removal & lowered Fe concentration, the combined system achieving complete color, 69% COD & appreciable salt removal. Al-electrode should be preferred to Fe-electrode to avoid residual Fe interfering reuse of wastewater for dyeing light colors.	43 (2001)
O <sub>3</sub> / Coagulation/ Activated sludge	Textile wastewater	Complete decolorization of the textile effluent (COD=1800 mg/l, JTU <sub>transparency</sub> =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.	127 (1993)
Coagulation/ Activated sludge/ Overland flow	Cotton textile wastewater	Input COD, TDS and Turbidity (2009 mg/l, 2987 mg/l, 102 NTU) reduced as follows: <b>After Physicochemical</b> [Alum <sub>416</sub> mg/l, lime <sub>213</sub> mg/l, polyelectrolyte <sub>11</sub> mg/l]: (1054 mg/l, 1540 mg/l, 52 NTU); <b>After Activated sludge</b> [HRT=20 hr, COD loading-0.9 kg COD/m <sup>3</sup> , MLSS-3073 mg/L, sludge recycle-20%]: (488 mg/l, 772 mg/l, 49 NTU); <b>After land treatment</b> : (89 mg/l, 239 mg/l, 20 NTU);	185 (1996)
Bio/ Electrochemical+H <sub>2</sub> O <sub>2</sub> / Coagulation/ Ion exchange	Dyeing & finishing wastewater	Electrochemical (DC 2.5A; 200 mg/l H <sub>2</sub> O <sub>2</sub> ; pH=3; 10 min) & coagulation (100 mg/l PAC, 1mg/l polymer) on biologically pretreated wastewater (COD= 111mg/l; Conductivity=4850 μmho/cm) achieved 72.8% COD & 97.3% color removal, while subsequent ion exchange (cationic=40, anionic=20g/l) reduced conductivity & COD to 10 μmho/cm & 10mg/l. [Reusable]	130 (1996)
Coagulation/ Activated sludge, AS/ Filtration/ Disinfection	Textile wastewater	[BOD <sub>5</sub> (mg/l), COD, Conductivity (μs/cm)]: Influent= [940, 2560, 3500]; After chemical treatment (FeSO <sub>4</sub> .7H <sub>2</sub> O= 0.72 kg/m <sup>3</sup> , Polyelectrolyte= 0.2 g/m <sup>3</sup> )= [512, 1250, 2940]; After tertiary = [15, 310, 2800], reusable for irrigation.	155 (1992)

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Bio ( <i>Phanerochaete chrysosporium</i> fungi) /O <sub>3</sub>	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 <sub>3</sub> treatment (pH=11, 15 l/h, 80 min.) accompanied by 40% decoloration in each step, the final effluent showing no toxicity.	115 (2001)
Bisulfite-catalyzed Na-borohydride reduction / Bio	Direct <sup>N=N</sup> red 23, Disperse <sup>N=N</sup> yellow 5, Acid <sup>N=N</sup> yellow 17, Basic <sup>N=N</sup> blue 41, Reactive orange 13	DYE: Depending on dye (200 mg/l), 85-98% decoloration within 10-30 min. by chemical reduction. <b>Actual wastewater (COD= 770 mg/l);</b> [COD & color removal]: i) Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> (200-250 mg/l)- catalyzed NaBH <sub>4</sub> (50-60 mg/l) reduction=[73-86%, 8-12%]; ii) Subsequent biological oxidation=[74-87%, 74-76%].	71 (2003)
Bio/ Photoreactor	Reactive (Cibacron red FB), Dispersal Yellow C-4R, Direct (Solphanyl Orange T4RL)	[COD removal, yellow/red color removal]: <b>Only biological</b> [HRT 3 days, SRT 20 days]: [60%, 10-15%/not significant]; <b>Only photoreactor</b> <sub>[4g TiO<sub>2</sub>/150 g zeolite, Light (365nm) intensity 30W/m<sup>2</sup>, 200hrs]</sub> : [>90%, completely decolorized], <b>Bio-photoreactor</b> <sub>[24 hr illumination]</sub> : [>90%; complete decolorization]	121 (1997)
Photochemical/ Bio (Fungi)	Kraft E1 effluent (containing lignin and colored compounds like quinones, chalcones, stilbenes)	<b>Only Photocatalysis</b> [50 mg sand-immobilized ZnO (10%,w/w) / 10ml effluent; Light (254nm) intensity=108W/m <sup>2</sup> ; pH=6.5; 2hr]: 100% decoloration, 80% CO <sub>2</sub> formation, 90% COD reduction; <b>Only Bio</b> = 57% decoloration; <b>Photo (10min)-Bio(Lentinula edodes fungi, 96hr)</b> : 73% decoloration.; <b>Bio (5d+3d, 2 cycles)-Photo (20min)</b> : 100% decoloration	178 (1998)
Thin-film photo-reactor containing photosynthetic bacteria	Acid <sup>N=N</sup> blue 92	TiO <sub>2</sub> -coated reactor irradiated with UV and fluorescent light (3 of each type @ 6W) facilitated decolorization efficiency (80%; 15 mg dye/gMLSS/d) of photosynthetic bacteria (without any inhibition induced by UV- radiation) by avoiding algal growth and its adhesion on reactor.	83 (2003)
Fe(III)/ photo (solar) assisted biological system	5-amino-6-methyl-2-benzimidazolone (AMBI); dye intermediate	The 300 min. (shortest possible to yield the best combined result) aerated, Fe (III)/light pretreatment (Fe <sup>+3</sup> =1mmol/l; 400W; 80mWcm <sup>-2</sup> ) achieved 100% AMBI (1mmol/l) degradation and 40% DOC removal, while subsequent immobilized biological column (6 l/h) completed the mineralization. Pilot scale investigation under solar radiation recommended Fe (III)/H <sub>2</sub> O <sub>2</sub> /light for 10 times faster reaction.	187 (2003)
Electron-beam treatment/Bio	Mixed raw wastewater predominantly from dyeing process & 8% from polyester fiber production	Pilot plant investigation (flowrate=1000 m <sup>3</sup> /d) involving low dose (1 kGy) E-beam pretreatment 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.	81 (2004)
AOP (Peroxon, O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> ; Photo-fenton with Ozone, O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> +UV+Fe <sup>+2</sup> ) / Bio	4,4'-dinitrostilbene-2,2'-disulphonic acid (DNS) <sup>C=C</sup> , fluorescent whitening agent precursor	[ <b>Initial</b> : COD= 2840 mg/l; BOD <sub>28</sub> /COD=0.04]. Peroxon (Molar ratio, DOC:O <sub>3</sub> :H <sub>2</sub> O <sub>2</sub> =1:1:1/3) or Photo-fenton with Ozone (DOC:O <sub>3</sub> :H <sub>2</sub> O <sub>2</sub> : Fe <sup>+2</sup> =1:0.3:1:1/20; UV 150w) realized similar 60% COD, 50% DOC & 60% AOX removal, while the biodegradation of the 5 times diluted pre-oxidized sample achieved overall 80% COD removal. Sole ozonation, however, achieved better decoloration than the above two. In situ .OH formation without need of UV recommended due to strong UV-absorbing compounds in this wastewater.	85 (2003)
Bio/ AOP (Peroxon, O <sub>3</sub> +H <sub>2</sub> O <sub>2</sub> ) / Bio	Stilbene <sup>C=C</sup> -based fluorescent whitening agent	[ <b>Initial</b> : COD= 1980 mg/l; BOD <sub>28</sub> /COD=0.44]. AOP pretreatment prior biological treatment did not have any improvement effect over sole biodegradation; hence a reversed sequence was adopted. Biological pretreatment removed 60% COD & 55% DOC, while the final biodegradation following the intermediate AOP (Molar ratio, DOC:O <sub>3</sub> :H <sub>2</sub> O <sub>2</sub> =1:1:1/3) treatment achieved an overall 84% COD & 71% DOC removal.	85 (2003)
Clariflocculation/Bio/AOP (H <sub>2</sub> O <sub>2</sub> /UV)	Wool scouring effluent	Clariflocculation followed by aerobic biological treatment removed >90% COD & all BOD; however, remaining COD (1000mg/l) & intense color warranted subsequent H <sub>2</sub> O <sub>2</sub> /UV [Molar ratio, COD: H <sub>2</sub> O <sub>2</sub> =1:1; 40w] treatment which, despite presence of strong UV absorbing compounds, achieved 100% decoloration (30 min), 75% COD & 85% TOC removal (60 min.) irrespective of pH.	170 (2004)
Bio/ Flocculation/ O <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	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 <sub>3</sub> + H <sub>2</sub> O <sub>2</sub> treatment (60 min.; [H <sub>2</sub> O <sub>2</sub> ]:[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).	126 (2004)
[O <sub>3</sub> ]/Bio/ [O <sub>3</sub> ]	Wastewater from plants dyeing & finishing natural/ synthetic fibers	Pre-ozonation, due to selective preference of O <sub>3</sub> for simpler organic compound, significantly decreased readily biodegradable COD without appreciably affecting soluble inert COD. Post-ozonation achieved higher color and inert COD removal involving 50% less ozone dose compared to pre-ozonation at same contact time & ozone flux rate.	158 (2002)
Bio/ Sand filter (SF)/ O <sub>3</sub>	Wastewater from plants dyeing &	Removal of suspended solid (& hence COD) by biological & SF pretreatment enhanced subsequent two sequences	43

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	finishing natural/ synthetic fibers	of ozonation (30 min., 40 g/m <sup>3</sup> ), achieving, in contrast to 60% COD removal by ozonation alone (without pre-treatment), a combined 65% & 78% COD removal after 1 <sup>st</sup> & 2 <sup>nd</sup> ozonation cycle, respectively. Complete decoloration allowed wastewater reuse in dyeing even light colors.	(2001)
Bio (Anaerobic/Aerobic)/O <sub>3</sub> / Bio (Aerobic)	Segregated concentrated dyebath containing C. I reactive Black 5 & high salt concentrations.	Although biological pretreatment achieved >70% decoloration, and ozonation increased biodegradability in following aerobic reactor, high ozone dose of 6gO <sub>3</sub> /gDOC was required to achieve combined >95% decoloration & 80% DOC removal while not more than 30% DOC was removed by biological reactor; internal recycle between ozonation & aerobic stage recommended for reducing ozone dose.	124 (2003)
Bio (anaerobic-aerobic)/ O <sub>3</sub>	Colored wastewater containing melanoidins	Ozonation (1.6 g/h- 11.5 g/h) of biologically (anaerobic-aerobic) pretreated wastewater (COD= 4580, TOC= 1000, mg/l) achieved 71-93% decoloration & 15-25% COD removal in 30 min.	165 (2003)
Bio (Anoxic/ aerobic) /O <sub>3</sub>	Reactive <sup>N=N</sup> black 5 (vinyl sulfonic acid), Reactive <sup>N=N</sup> red 198 (vinyl sulfonic acid & triazine), Remazol Dunkelblau HR (Metalized azo) <sup>N=N</sup> , Remazol Goldgelb RNL <sup>N=N</sup> , Reactive <sup>N=N</sup> yellow 25 (Dichloroquinoxaline), Reactive <sup>N=N</sup> Red159 (Dichlorofluoropyrimidine)	Sequencing anoxic/ aerobic process along with partial oxidation by ozonation (concurrent with aerobic phase) in a recirculated system yielded complete decoloration and showed synergistic enhanced biological DOC removal (90%) as well as lower consumption of O <sub>3</sub> (5 mg/ mg DOC).	111 (1998)
Biological+physico-chemical/ O <sub>3</sub>	Jeans finishing plant wastewater mixed with domestic WW (<30%)	Pretreatment involving GAC (200g/8L) & polyelectrolyte addition in anaerobic reactor restored nitrification activity & improved sludge settleability of the subsequent aerobic reactor with a cumulative 96% COD & 88% color removal, while following ozonation achieved 70% reusable water.	205 (1999)
Bio /O <sub>3</sub>	Naphthalene-1,5-Disulphonic Acid (NADSA), a dye precursor	Combined fixed-bed bioreactor (equipped with a 1.5µm membrane for solid/liquid separation) and ozonation treatment in semi-continuous fashion achieved ca. 80% DOC removal (Initial= 170-340 mg/l) with >50% reduction in ozone consumption (0.8 mol O <sub>3</sub> /mol DOC) as compared to single use of ozonation only.	30 (2003)
Bio/O <sub>3</sub> /Granular activated C(GAC)	Domestic + Textile industry (50-70%) wastewater	<b>Feed water</b> [on GAC]: COD= 128-135 mg/l, TOC=16-18 mg/l; C-adsorption is less effective after the ozonation, residual COD (> 70) & color (over optical detection) unsuitable for reuse; "Bio+Flocculation+O <sub>3</sub> +GAC" proposed.	23 (1999)
O <sub>3</sub> /Biological activated C (BAC)	Natural coloring matter (Humic substances)	Biodegradable DOC increased by pre-ozonation was subsequently biodegraded rather than being simply adsorbed on BAC and, thereby, increased BAC service time.	221 (1997)
Coagulation or Catalytic H <sub>2</sub> O <sub>2</sub> / Bio	Basic dye	Chemical precipitation (FeCl <sub>3</sub> = 400 mg/l; pH=9.5), despite resulting in 41% COD removal from raw wastewater, could not improve biodegradability. After partial oxidation (H <sub>2</sub> O <sub>2</sub> /COD=1; Fe <sup>+3</sup> = 500 mg/l; pH= 3.5; 1day) 63% COD removal & wastewater-biodegradability was achieved.	15 (1999)
Biological fixed GAC bed	Acid <sup>N=N</sup> (Tectilon Red 2B, Tectilon orange 3G)	GAC bed inoculated with special chromophoric bond-cleaving & aromatic ring- cleaving bacteria, after initial acclimatization period, outperformed conventional GAC bed; the bacterial activity, however, decreased after certain period due to lack of nutrient and/or dissolved oxygen. [Dye= 100 mg/l].	218 (1996)
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, color, COD, & NH <sub>3</sub> -N removal with concurrent prolonged carbon-bed life, the performance essentially being better than normal BAC or pure GAC process.	177 (2004)
Biological fluidized GAC bed	Bleached kraft mill secondary effluent containing refractory organics like lignin, which may be considered to be representative of dye structure.	57% DOC removal (initial = 280-330 mg/l; 0.9 g DOC/ kg AC. d) by physical adsorption on GAC and biomass followed by biodegradation & desorption achieving partial bioregeneration of GAC was observed. Combined 'bioregeneration/ physical (US-IR)-partial regeneration (50% of GAC volume)' achieved 30-40% improved removal with 2% weight loss/regeneration, which is smaller than loss due to sole regeneration by physical method.	217 (1994)
Bio+ Recirculated Powdered activated C (PAC) / Flocculation	Domestic effluent mixed with Reactive dye (Cibacorn yellow CR01, Cibacorn yellow F3R, Ci-	[Initial COD= 775-4035, pH= 9-12]; Recirculation of PAC (13 mg/l) resulted in effective removal of dyes and halogenated/refractory organics along with optimum use of PAC which is only partially loaded if not recycled.	156 (1999)

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	bacorn red C2G, Cibacorn red CR, Cibacorn Red FB, Cibacorn blue FB, Levafix yellow KR, Levafix red KGR, Remazol red, Remazol black) /salts/auxiliary chem.		
Powdered activated carbon or organic flocculant addition in biological system	Cotton textile wastewater	<b>Only Bio</b> (SRT= 30 days, HRT=16 days): 94% COD removal, 36% decoloration. <b>Combined</b> (PAC=200 mg/l or Organic flocculant= 120 mg/l): Decoloration improved up to 78%, the organic flocculant producing less excess sludge than PAC.	161 (2002)
Powdered activated carbon addition in biological system (PACT)	Acid <sup>N=N</sup> orange7, C.I. 15510	The behavior of COD removal was the same but the dye removal was better in the PACT than in the conventional activated sludge process.	49 (1997)
Powdered activated carbon addition in biological system	Acid <sup>N=N</sup> orange7, C.I. 15510	Under a higher biomass concentration (> 3g/l), the carbon particles are trapped in the floc matrix and lose their properties of adsorption hindering microbial growth and dye removal.	141 (1997)
Powdered activated carbon addition in biological system	Dispersed, direct, acid & basic dyes; anionic/nonionic detergents.	Removal efficiency rises from 55.8 to 75.6% (COD) and from 78 to 98.5% (TOC). The nitrification- denitrification capacity of the system also increases, probably due to high concentration of nitrifying-denitrifying bacteria on the PAC surface.	197 (1984)
Fluidized bed reactor containing complex pellets of white rot fungus & activated carbon	Acid <sup>N=N</sup> violet 7	Complex mycelium pellets with a black core of activated carbon (preparation: 5ml inoculum+ 0.6 g A.C+200ml medium), by retaining necessary fungal metabolites, outperformed standalone application of fungi or activated C, or even simple addition of activated C in fungi reactor; the decoloration (95%) being better in repeated batch reactor (50 g wet complex pellet/L; 20 hr retention; 500 mg/L dye) than in continuous reactor.	235 (2000)
Activated Carbon (AC)- amended anaerobic bioreactor	Hydrolyzed reactive <sup>N=N</sup> red 2, Acid <sup>N=N</sup> orange 7	AC, in addition to its adsorption capacity, as a biologically regenerable redox mediator due to quinone surface group on it, enhanced azo dye reduction, achieving 97-90% decoloration for 130 days [42 mg/L dye; 35g/L VSS; HRT=5.5 hr; 10 g/L AC].	234 (2003)
Bio/ NF	Diluted wool dyeing bath containing metal complex & acid dye (original dye concentration 8g/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% color & 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.	33 (2001)
Bio/Membrane(+Aluminum polychloride)	Domestic + Textile industry (80% by organic load) wastewater	Microfiltration (300,000 D, crossflow) followed by nanofiltration (150D, 10 bar, spiral wound) along with Aluminium polychloride (70 mg/l) produced recyclable water (COD<10 mg/l, conductivity < 40us/cm, negligible residual color) from the secondary effluent; alternately "Clariflocculation (Dose: 4ppm, vol.) + Multimedia filtration+ Low-Pressure RO (58 D,4 bar, 10L/m <sup>2</sup> .h, spiral wound)" seemed preferable in techno-economical analysis.	183 (1999)
'Bio+ Powdered activated C, (BPAC)'/ Microfiltration	Secondary sewage effluent containing refractory organics like lignin which may be considered to be representative of dye structure.	PAC dose of 0.5g/l. 52% TOC removed in BPAC contactor (higher than PAC only), additional 16.8% was rejected by membrane.	189 (1997)
Bio/ NF or O <sub>3</sub>	Wastewater from printing, dyeing & finishing textile plant	<b>Biologically treated:</b> Conductivity (mS/cm) 2.8-3.33; COD (mg/L) 200-400. <b>Following biological treatment</b> i) <b>Nanofiltration</b> (flow rate =200-400 L/h, TMP=20 bar): COD<50 mg/l; Conductivity =0.39-0.51 mS/cm. ii) <b>O<sub>3</sub></b> : COD=286 (30 min.), 70 (210min.) iii) <b>O<sub>3</sub>+UV</b> : COD <50 (30 min.), <50 (210 min.). Ozonated (with/without UV) wastewater can't be reused for rinsing due to negligible conductivity removal although the process is free from reject stream generation.	27 (2003)
Bio/ NF/ O <sub>3</sub>	Textile wastewater mixed with domestic (20%) wastewater	Ozonation (12 ppm, 2hrs.) of membrane-concentrates (COD= 595, TOC=190, Conductivity=5ms/cm, BOD <sub>5</sub> =0, EC <sub>20</sub> =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.	134 (1999)
Bio/ NF/ Photocatalytic membrane reactor	Textile wastewater	Visible Light mediated Fenton (Nafion-Fe <sup>+3</sup> membrane, 1.78%; H <sub>2</sub> O <sub>2</sub> , 10mM) treatment (3 hrs.) of membrane-concentrates (COD= 496, TOC=110, pH= 8) resulting from nanofiltration of biologically treated secondary textile	17 (1999)

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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 <sub>3</sub>	Textile wastewater mixed with domestic (25-30%) wastewater	Due to cost of membrane and, COD & salinity increase in biological plant by membrane retentate, techno-economical analysis favored 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, colorless) recyclable effluent.	182 (1999)
Bio/ Sand filtration (SF)/ Membrane (MF followed by NF)	Dyeing wastewater	100% SS, 78% turbidity & 30% COD removal by SF (2 bar) & MF (3.5 bar; 400 l/h); 13% color removal by MF, and remaining COD & color removal by NF (6.5-7 bar) contributed to overall 94% color & 82% COD removal along with conductivity removal making the treated water reusable for dyeing.	139 (2002)
Membrane filtration (NF)/ UV-H <sub>2</sub> O <sub>2</sub> /Wet Air Oxidation (WAO)/ Bio (Immobilized)	Textile wastewater	Reuse of wastewater after membrane filtration and advanced oxidation process, concurrent with reuse after membrane concentrate treatment by WAO and Biological treatment, thereby enabling an affordable zero-discharge system.	120 (2001)
PAC+MBR (Rotating UF Membrane)	Wastewater in a sewage treatment plant with humic substances as major component of color.	PAC (50 mg/l, retention time of 4.5 hrs.) addition in anaerobic reactor followed by an aerobic reactor coupled with a rotating type UF membrane resulted in a color of less than 5 deg., BOD=0, TOC<10 with simultaneous improvement in activated sludge dewaterability and reduction of filtration resistivity.	157 (1998)
Anaerobic/ Aerobic 1/ Aerobic 2 ( MBR) / Ozonation	Reactive azo dye containing wastewater [Stream a (40%)- dyeing/ color preparation/ printing; Stream b (60%)- fiber pretreatment, washing]	Stream-a, after anaerobic/aerobic pretreatment, was discharged into municipal wastewater. For Stream-b, the mean combined DOC & color removal after anaerobic, aerobic 1, MBR and ozonation (1g O <sub>3</sub> m-3m1) were [53%, 65%, 87%, 87%]DOC & [67%,65%,72%,87%]color, respectively and hence could be reused.	112 (2004)
Sidestream UF membrane fungi reactor	Colored wastewater containing melanoidins	With a HRT of 2d in a 1-d cycle sequencing batch mode, under a pH of 4.5, temperature of 30°C and otherwise non-sterile condition, about 70% decolorization was achieved using the entire system (fungi+UF) while fungi reactor alone contributed 45%.	62 (2000)
Submerged MF membrane fungi reactor	Synthetic wastewater containing Poly <sup>N=N</sup> S 119	With a HRT of 15 hrs., under a pH of 4.5, temperature of 28°C and otherwise non-sterile condition, stable 98% decoloration and 97% TOC removal was achieved. Tremendous membrane fouling problem was solved by using innovative fouling amelioration techniques.	78 (2005)
Prefiltration (8000 Da, 1 Mpa) followed by airlift fungal reactor equipped with submerged coarse filter (50µm)	Kraft mill bleaching effluent (acidic, C+D; alkaline, E)	C+D-stage effluent mixed with membrane filtrate of E-stage effluent in 4:1 ratio (Net 13% AOX, 32% COD, 27% TOC, 44% color removal, after mixing) was submitted to subsequent fungi treatment (HRT=22 h; 0.77 kgTSSm-3) which achieved a combined 39% AOX, 62% COD, 56% TOC, 56% color removal. Unexpected inferior performance of fungi reactor was ascribed to use of biomass not adapted long enough.	29 (1991)

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**Table 5. Cost information pertaining to different combinations**

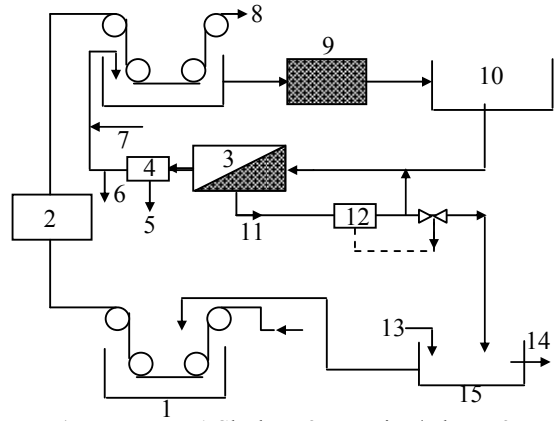
Purpose & Technology	Cost	Dye / Wastewater	Remarks	Ref. (Year)
Direct nanofiltration for reuse	US\$ 0.53-1.19 <sup>a</sup> m <sup>-3</sup>	Segregated dyeing and rinsing wastewater	Running cost (15 bar, flow rate= 4.5 m/s, flux= 0.2-1.1 m <sup>3</sup> /h) only; saving of water supply cost due to recycling not considered.	215 (2001)
Direct nanofiltration for reuse	US\$ 0.81 m <sup>-3</sup>	Wastewater from dye bath containing acid, disperse and metal complex dye	Cost includes both capital & operating cost (Flow rate= 1000 m <sup>3</sup> /d). Saving of water supply cost (2-3 US\$m <sup>-3</sup> ) due to recycling not considered.	108 (2001)
Direct nanofiltration for reuse of water and dye bath salt	US\$ 1.36 m <sup>-3</sup>	Reactive dye bath wastewater containing high amount of NaCl	Flowrate = 200 m <sup>3</sup> /d; quoted cost has been calculated using the operating and investment cost mentioned in the reference (assuming 10 yr investment). A payback of investment cost may be expected in less than 2 yrs with the saving of water supply cost, wastewater disposal cost, NaCl and heat energy.	110 (2004)
Reuse of water and chemical residues by (i) Membrane filtration, (ii) Chemical precipitation, (iii) Activated C, (iv) Counter-current evaporation	US\$ m <sup>-3</sup> (i)1, (ii)1-2, (iii)10-15, (iv) 10-15	Reactive dyeing of cotton	Cost includes operating and investment cost.	219 (1996)
Electrocoagulation as sole treatment	US\$ 0.1-0.3 (kg COD removed) <sup>-1</sup>	Mixture of exhaust dyeing solutions	Operating cost (including energy and material cost) for iron and aluminium electrode, respectively. Labour, maintenance and solid/liquid separation cost not considered. [Wastewater COD= 3422 mg/l; around 70% removal.]	21 (2004)
Combined treatment with H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> /UV	US\$ 6.54 m <sup>-3</sup>	Wastewater containing disperse dyestuff & pigments	Cost of consumables only. Less yet satisfactory (>90%) COD removal by Fenton's reagent at a lower (0.23 US\$) unit cost.	12 (2004)
Combined treatment with O <sub>3</sub> /Electron beam to meet discharge standard	US\$ 3.17 m <sup>-3</sup>	Molasses processing wastewater (intensely colored and recalcitrant)	Cost includes both capital & operating cost (Flow rate= 50 m <sup>3</sup> /hr).	69 (1998)
Combined treatment with multi-stage Coagulation/ O <sub>3</sub>	1.57 <sup>c</sup> US\$ ton <sup>-1</sup> h <sup>-1</sup>	Dye manufacturing wastewater	Approximate cost considering electricity cost of ozone generation only (chemical cost made small contribution).	86 (1998)
Combined treatment with adsorption +UV- H <sub>2</sub> O <sub>2</sub>	US\$ 1 m <sup>-3</sup>	Reactive Everzol Black-GSP	Operating cost (consumables and maintenance) for decoloration & 50% TOC removal from 36 ppm dye solution.	91 (2002)
Combined treatment with Clariflocculation/Ozonation/ Membrane (UF) for reusable water	US\$ 0.52 <sup>b</sup> m <sup>-3</sup>	Wastewater from carbonizing, dyeing and fulling process	Flowrate = 1500 m <sup>3</sup> /d; Cost includes operating and investment cost. A payback of investment cost may be expected in 3 yrs with the saving of water supply cost.	139 (2002)
Photo (solar)-fenton pretreatment (for subsequent biological treatment)	US\$ 22 m <sup>-3</sup>	Dye-intermediate (5-amino-6-methyl-2-benzimidazolone AMBI) containing wastewater; 4 g C/L	Cost (for 1.2 Lh <sup>-1</sup> m <sup>-2</sup> ) includes annualized capital, consumables & maintenance but excludes high land cost (US\$ 200-400 m <sup>2</sup> ) in Switzerland. Economical than wet air oxidation or incineration (US\$ 200m <sup>-3</sup> ). Further cost reduction possible for diluted wastewater at a location providing higher sunny hours.	187 (2003)
Coupled Photo -fenton and biological treatment	US\$ 71 m <sup>-3</sup>	<i>p</i> -nitrotoluene- ortho- sulfonic acid (contained in dye manufacturing wastewater), 1 g/L or 330 mg C/L	Cost of 70 min. (0.68 L/h) photo-fenton pretreatment using 400 W lamp (0.12 US\$/ KWH) prior to biological treatment, combined DOC removal being 91%. Commercial lamps, being far more efficient, would incur less cost.	175 (1999)
Combined treatment with O <sub>3</sub> / Bio (Aerobic, Rotating disc reactor)	US\$ 94.7 <sup>b</sup> m <sup>-3</sup>	Segregated concentrated dye-bath containing C. I reactive Black 5 & high salt concentrations.	Cost includes both capital & operating cost (flow rate=50L/h). Higher value as compared to those from other studies e.g. membrane separation (11.68 US\$ m <sup>-3</sup> ), adsorption followed by aerobic biological treatment (2.6 US\$ m <sup>-3</sup> ), precipitation/flocculation followed by activated carbon adsorption (5.19 US\$ m <sup>-3</sup> ) indicates the ambiguity arising from straightforward comparison of costs of segregated vs. mixed streams.	124 (2003)
UV/ H <sub>2</sub> O <sub>2</sub> treatment of secondary textile effluent to meet discharge	US\$ 0.85m <sup>-3</sup>	Textile wastewater	Operating cost including lamp replacement, chemical and electrical cost. (Discharge standard: COD<100 mg/l; color<400 ADMI unit)	123 (2000)

standard				
Post treatment of secondary textile effluent by (i) Ozonation, (ii) Membrane filtration	US\$ m <sup>-3</sup> (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 <sup>3</sup> /d; (b) 1000 m <sup>3</sup> /d.	108 (2001)
Combined treatment with Coagulation/ Electrochemical oxidation/ Activated sludge	US\$ 0.34 ton <sup>-1</sup>	Textile wastewater containing 15 dyes used in a plant making primarily cotton and polyester fibers and small quantity of wool	Mainly cost of consumables included. Economical than the conventional treatment process (US\$ 0.45 ton <sup>-1</sup> ) used at that time in Taiwan.	129 (1996)
Combined treatment with Coagulation/ Fenton's reagent/ Activated sludge	US\$ 0.4 m <sup>-3</sup>	Textile wastewater	Running cost, excluding that for sludge disposal. Economical than the conventional treatment process used at that time.	128 (1995)
Combined treatment with Coagulation/ Activated sludge / Filtration/ Disinfection	US\$ 0.19- 0.22 m <sup>-3</sup>	Textile wastewater	Operating cost (consumables and maintenance)	155 (1992)
Combined treatment with Bio/ Sand filter (SF)/ O <sub>3</sub> for reusable water	US\$ 0.13 <sup>b</sup> m <sup>-3</sup>	Wastewater from plants dyeing & finishing natural/ synthetic fibers	Cost mentioned is for operation & maintenance. Including investment cost, it may amount up to 0.52 US\$ m <sup>-3</sup> 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 <sup>-3</sup> ).	43 (2001)
Combined treatment with Bio/Clariflocculation/GAC for reusable water	US\$ 0.454 <sup>b</sup> m <sup>-3</sup>	Textile wastewater mixed with domestic (25-30%) wastewater	Flowrate = 25000 m <sup>3</sup> /d. Cost includes both capital & operating cost.	182 (1999)
Combined treatment with Bio/Membrane (MF→NF)/O <sub>3</sub> for reusable water	US\$ 1.69- 1.95 <sup>b</sup> m <sup>-3</sup>	Textile wastewater mixed with domestic (25-30%) wastewater	Flowrate = 25000 m <sup>3</sup> /d. Cost includes both capital & operating cost. The system may potentially become cost-effective with decline in membrane cost, the main cost-contributing factor.	182 (1999)
Combined treatment with Bio/ Sand filtration (SF)/ Membrane (MF followed by NF) for reusable water	US\$ 0.44 <sup>b</sup> m <sup>-3</sup>	Dyeing wastewater	Flowrate = 1500 m <sup>3</sup> /d; Cost includes operating and investment cost. A payback of investment cost may be expected in 3 yrs with the saving of water supply cost.	139 (2002)
Combined treatment with Bio/ Sand filtration (SF)/ Membrane (UF followed by RO) for reusable water	US\$ 1.26 <sup>b</sup> m <sup>-3</sup>	Wastewater from plants dyeing & finishing natural/ synthetic fibers	Flowrate = 1000 m <sup>3</sup> /d; Cost includes both operating and investment costs.	44 (2001)
Combined treatment with deep aeration activated sludge/ BAC/Membrane (NF) for 50% recycling	US\$ 0.294 <sup>c</sup> m <sup>-3</sup>	Wastewater from plants dyeing & finishing synthetic fibers	Flowrate = 50 m <sup>3</sup> /d; Cost mentioned is for operation & maintenance.	224 (2005)
Combined treatment with Bio/ Sand filtration (SF)/ Ozonation for 50% recycling	US\$ 0.57 <sup>b</sup> m <sup>-3</sup>	Wastewater from plants fulling & dyeing natural/ synthetic fibers	Flowrate = 2000 m <sup>3</sup> /d; Operating cost only. Required fresh water supply (50% of total) incurs a further cost of 0.92 US\$ m <sup>-3</sup> .	42 (2001)
Reuse after Membrane filtration (i), followed by UV/H <sub>2</sub> O <sub>2</sub> (ii), concurrent with reuse after membrane concentrate treatment by Wet air oxidation (iii) and Biological (iv)	US\$ m <sup>-3</sup> (i) 0.53 (ii)2.6 (iii)4.4 (iv)0.13	Textile wastewater	Flow rate= 400 m <sup>3</sup> /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.	120 (2001)
Membrane bioreactor	US\$ 0.273 m <sup>-3</sup>	Municipal wastewater <sup>d</sup>	Flowrate = 2.4 m <sup>3</sup> /h; cost mentioned includes all sorts of capital & operating costs. With expected decline in membrane cost to US\$ 50 m <sup>-2</sup> in 2004, the unit cost would reduce to US\$ 0.181 m <sup>-3</sup> .	228 (2004)

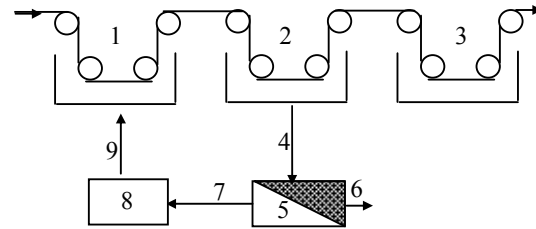
<sup>a,b,c</sup> Original reported values in Deutsche Marks, Euro and Taiwanese dollar have been converted to US\$ by multiplying with a factor of 0.663348, 1.29730, 0.0322134, respectively. <sup>d</sup> Data given for comparison of MBR technology with others only.

Fig.2 Different stages of textile wet processing and associated scopes of material recovery<sup>127,220</sup>

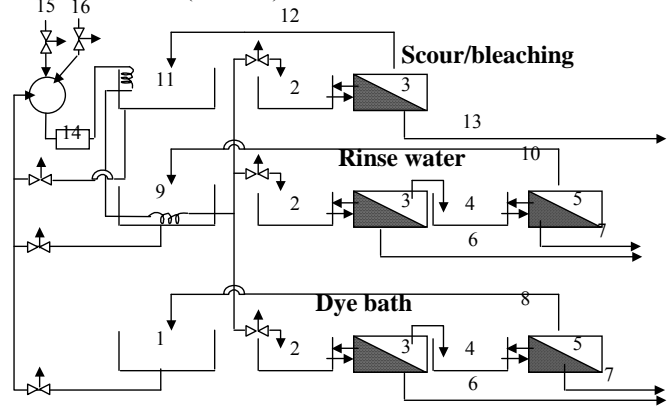
Process	Purpose and Chemical additives/drainages
Slashing/ Sizing	Cotton or synthetic threads are treated with a large amount of reusable thickening agent (Poly Vinyl Alcohol, PVA) to impart tensile strength and smoothness.
Desizing	To allow further wet processing, PVA is removed with a weak oxidizing agent, boiling water/detergent.
Scouring	Impurities in natural fibers (grease, wax etc.) or in synthetic fibers (catalysts, low molecular weight compounds etc.) are removed using caustic -soda/ash, detergent etc.
Bleaching	Naturally occurring pigments are removed using peroxide and caustic.
Mercerizing	Cotton is treated with concentrated caustic to correct curling of fiber, reducing shrinkage and increasing dye affinity, following removal of the added chemical by warm water/detergent wash.
Weight reduction	Polyester fiber is treated with caustic, following its removal by hot and cold-water wash, whereupon 10-20% of weight of fiber is expelled as organic acid.
Dyeing and rinsing	Different types of dyes along with wide range of dyeing-auxiliaries, e.g., electrolyte, dispersing agent, smoothing agent, surfactants etc. are applied. Hot water/detergent rinse is applied to remove unfixed dye and auxiliaries.
Oiling	To increase the cohesion of the fibers and aid in spinning, olive oil/ mineral oil with non-ionic emulsifier is sprayed on wool, and washed out later on.
Fulling	Loosely woven wool from the loom is shrunk into a tight, closely woven cloth using detergent, caustic, sequestering agent, which are washed out later on.
Carbonizing	Using hot concentrated acid the vegetable matter in the wool is converted to loose, charred particles, which are mechanically shaken out; finally carbonized wool is neutralized.
Printing and rinsing	Cotton and synthetic fiber. Similar to dyeing/ rinsing.
Finishing	Chemicals are added to render anti-bacterial deodorants, water resistance, stain proofing, glossiness etc. Involves less water and related drainage.



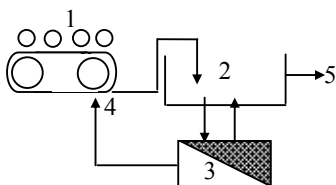
**PVA recovery:** 1.Slasher, 2.Weaving/others, 3.UF membrane, 4.Permate tank, 5.Periodic wash out, 6.Heat recovery, 7.Water make-up, 8.To further processing, 9.Screens, 10. Buffer Tank, 11.Concentrate, 12.Refractometer, 13.PVA make-up, 14.Periodic wash out, 15.Mixing tank



**Caustic recovery (Mercerizing):** 1.Mercerizing (25% NaOH), 2.Warm water wash, 3.Hot water wash, 4. Contaminated NaOH(6%), 5.Membrane, 6.Concentrate(Fibers, washing agent), 7.Purified NaOH(6%), 8.Evaporator, 9.Clean NaOH(18-25%)

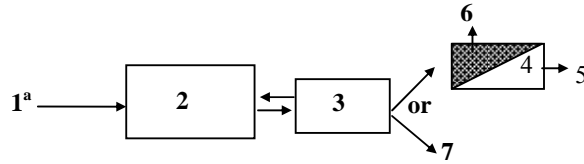


**Full recycle/ Jet dyeing machine:** 1.Dye-bath water, 2.UF process tank, 3.UF membrane, 4. NF process tank, 5.NF Membrane, 6.Disperse,Sulfur,Vat,Acid dye 7.Reactive,Direct,Cationic dye 9.Rinse water, 10.Water, 11.Scour/bleaching water, 12.Water, peroxide,detergent,13.UF membrane, 14.Prefilter, 15.Brine, 16.Caustic



**Printing:** 1.Print machine, 2.Concentrated waste, 3.UF membrane, 4. Clean water, 5.Periodic disposal

Fig.3 Layout of a conceptual on-site textile dye wastewater treatment scheme (*Continuation from Fig. 2*)



**Integrated MBR-AOP-Membrane treatment scheme**

1.Wastewater<sup>a</sup>; 2.Membrane separated fungi reactor; 3.Solar photocatalytic reactor; 4. RO membrane; 5,7.Recyclable water; 6.Concentrated salt

<sup>a</sup> For an integrated textile processing plant the wastewater is composed of the concentrate and discarded streams after possible material recoveries (refer to Fig.2), 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.