

Effective Treatment Systems for Azo Dye Degradation: A Joint Venture between Physico-Chemical & Microbiological Process

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Abstract Practically most of the accepted 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.

Keywords: waste water, decolorization, hybrid treatment systems, energy and water, reuse

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1. Introduction

Even though we can travel to the Moon, send robots to Mars, make super computers and clone organisms we still have difficulties to clean the water we use. In many parts of the world the availability of water is a crucial issue, and even more so, clean water. Environmental pollution is the most horrible ecological crisis that man is facing today. Pollution is a global threat to the environment and it becomes a scare word of today's world. The rapid growth of human populations fuelled by technological developments in health and agriculture has led to a rapid increase in environmental pollution. The unprecedented population increase and industrial development during the 20th century has not only increased conventional solid and liquid waste pollutants to critical levels but also produced a range of previously unknown pollution problems for which society was unprepared. The growth of the world population, the development of various industries, and the use of fertilizers and pesticides in modern agriculture has overloaded not only the water resources but also the atmosphere and the soil with pollutants [1,2,3,4,5]. In the last few decades the handling of wastewater appeared to be one of the most important. The degradation of the environment due to the discharge of polluting wastewater from industrial sources is a real problem in several countries. This situation is even worse in developing countries like India where little or no treatment is carried

out before the discharge [6]. The environmental problems created by the textile industry have received increased attention for several decades because this industry is one of the largest generators of contaminated effluents [7], which mainly arise from dyeing and finishing processes and is associated with the water pollution caused by the discharge of untreated or poorly treated effluents. Wastewater resulting from these processes has adverse impacts in terms of Total Organic Carbon (TOC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), suspended solids, salinity, colour, a wide range of pH (5–12) and the recalcitrance of organic compounds, such as azo dyes [8,9,10,11,11]. The ratio of BOD/COD ranges from 0.2 to 0.5 and indicates that these effluents contain a large proportion of non-biodegradable organic matter [8,12]. For example, 0.6–0.8 kg NaCl, 30–60 g dyestuff and 70–150 L water are necessary to dye 1 kg of cotton with reactive dyes; the wastewater produced has 20–30% of the applied unfixed reactive dyes, with an average concentration of 2000 ppm, high salt content and dyeing auxiliaries [13]. Worldwide, 280,000 tons of textile dyes are discharged in industrial effluents every year [14], and the main concerns involve the adverse effects of azo dyes in the environment, including their inhibitory effect on aquatic photosynthesis, ability to deplete dissolved oxygen, and toxicity to flora, fauna and humans. If the dyes are broken down anaerobically, aromatic amines are generated, which are very toxic, carcinogenic and mutagenic. Azo dyes are the most widely used dyes and represent over 60% of the total dyes

[15]. They are complex aromatic compounds with significant structural diversity. Their properties are enhanced to provide a high degree of chemical, biological and photocatalytic stability and resist breakdown due to time, exposure to sunlight, microorganisms, water and soap; in other words, they are resistant to degradation [8]. Furthermore, the reductive cleavage of azo linkages is responsible for the formation of amines, which are classified as toxic and carcinogenic [16]. Synthetic dyes cannot be efficiently decolourised by traditional biological processes [17]. Thus, a number of biological and physicochemical methods have been developed for the efficient removal of industrial azo dyes [18,19,20]. Due to a general concern about the treatment of wastewater, the laws are becoming more stringent, a large number of investigations have been recently developed to find more efficient methodologies for the treatment of wastewater, and microorganisms have been selected for the development of textile wastewater treatments. 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. 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 (Figure 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.

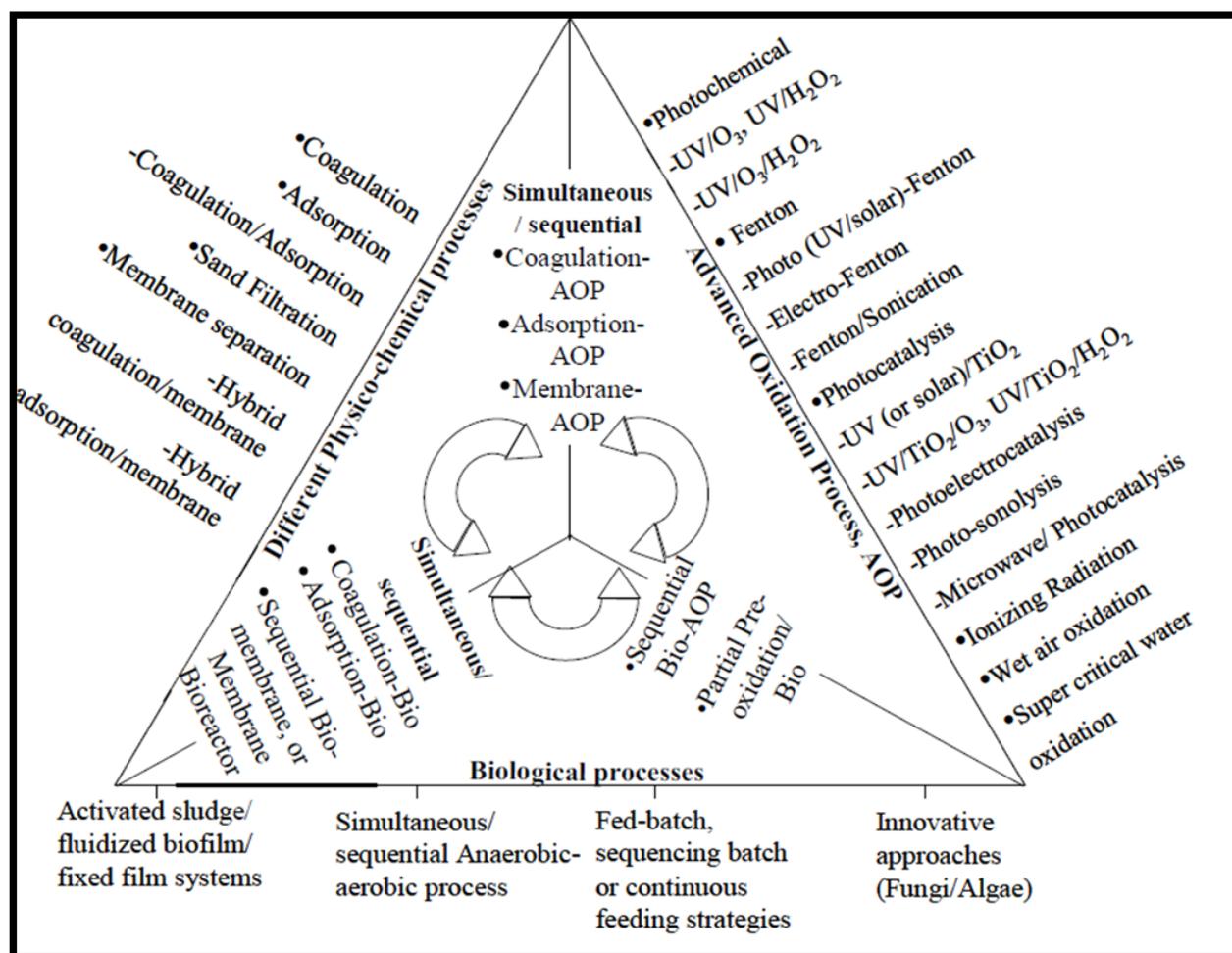


Figure 1. Simplified representation of broad spectrum of combinations proposed by many workers

Table 1. Advantages & Disadvantages of Treatment Systems

Sl.No.	Process	Advantages	Disadvantages	References
A.	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	Pagga and Taeger (1994)
B.	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	Fu and Viraraghavan (2001), Hao et al. (2000), Robinson et al. (2001)
C.	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	Fu and Viraraghavan (2001), Hao et al. (2000), Robinson et al. (2001)
D.	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	Robinson et al. (2001), Slocker and Marechal (1998)
E.	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	Robinson et al. (2001), Slocker and Marechal (1998)
F.	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	Robinson et al. (2001), Slocker and Marechal (1998)
1.	UV/O ₃	Applied in gaseous state, no alteration of volume. Good removal of almost all types of dyes; especially suitable for reactive dyes. Involves no sludge formation, necessitates short reaction times	Removal is pH dependent (neutral to slightly alkaline); poor removal of disperse dyes. Problematic handling, impose additional loading of water with ozone. Negligible or no COD removal. High cost of generation coupled with very short half-life and gas-liquid mass transfer limitation; suffer	Fu and Viraraghavan (2001), Gogate and Pandit (2004 I/II), Hao et al. (2000), Ince et al. (2002), Marachel et al. (1997), Robinson et al. (2001)
2.	UV/H ₂ O ₂	Involves no sludge formation, necessitates short reaction times and reduction of COD to some extent may be possible	Not applicable for all dye types, requires separation of suspended solid and suffers from UV light penetration limitation. Lower pH required to nullify effect of radical scavengers	Gogate and Pandit (2004I/II), Marachel et al. (1997)
3.	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	Hao et al. (2000), Marachel et al. (1997), Robinson et al. (2001)
4.	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)	Konstantinos and Albanis (2004)
5.	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	Chen (2004), Robinson et al. (2001)

Advanced Oxidation Processes (AOPs) have been studied broadly both for recalcitrant wastewater in general and dye wastewater in particular, their commercialization has yet not been realized because of prevailing barriers.[21,22] These processes are cost prohibitive and complex at the present level of their development.[23] 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 [24,25,26]. Although the usual small-scale laboratory investigations reveal encouraging results, such studies are insufficient to cast light on practical feasibility of AOPs. Only a handful of pilot plant explorations with less than

persuasive [27,28] or moderate [29] 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. 46 For the AOPs, the basic reaction mechanism is the generation of free radicals and subsequent attack by these on the pollutant organic species. Hence it is strongly believed that their combination will result in more free radicals, thereby increasing the rates of reactions [22,30]. 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.

Table 2. List of Different Treatment for Dye Waste Water

Different dye chromophores: ^{NN} : Azo, ^{AQ} : Anthraquinone, ^{TPM} : Triphenylmethane dye, TH : Thiazine, ^{XN} : Xanthene; ^{C=C} : Stilbene dye; ^{TC} : Phthalocyanine	Technology	Dye/ Wastewater	Details	Ref (Year)
	UV/O ₃	2-naphthalenesulfonate [Azo Dye intermediate]	Mineralization of 2-NS via ozonation (40 mg/l) is remarkably enhanced by UV radiation (60.35 W/m ² , 254 nm), tripling the rate. Not much difference in 2-NS decomposition.	31 (2002)
	UV/O ₃ , UV/H ₂ O ₂	Acid ^{NN} - red 1/ black 1/ red14/ red 18/ orange 10/ yellow 17/ yellow 23; Direct ^{NN} yellow 4	Decoloration (20 mg/l dye): 100% in 10 min. by O ₃ (6 l/min. O ₂) with/without UV; 80% in 25 min. by H ₂ O ₂ -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.	27 (1995)
	UV/H ₂ O ₂	Hispanin Black CA [Direct ^{NN} Black 22]	UV (125 W)-H ₂ O ₂ (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.	32 (2002)
	UV/H ₂ O ₂	Acid dye [orange 8 ^{NN} / blue 74 ^{C=C} , Methyl orange ^{NN}]	Removal by Only UV (15W, 253.7 nm, incident photon flux = 6.1x10 ¹⁸ Einstein s ⁻¹ , 4.54≤pH≤5.5) and only H ₂ O ₂ in absence of UV was negligible. Combined: Decolorization rate rises by increasing the initial dosage of H ₂ O ₂ up to a critical value ([H ₂ O ₂]/[dye]=50-70) beyond which it is inhibited.	33 (2003)
	UV/H ₂ O ₂	Reactive- red 120 ^{NN} / black5 ^{NN} / yellow 84 ^{NN}	UV (15 W) / H ₂ O ₂ (optimum dose 24.5 mmol/l): 15 min.: [Decolorization>65%, COD removal= 40-70%], 60 min.: [Decolorization> 99%]; Degradation by products unobjectionable.	26 (2002)
	UV/H ₂ O ₂ and solar/H ₂ O ₂	Chlorotriazine Reactive ^{NN} Orange 4	Dye removal (0.5 mmol/l), 150 min., pH 3: UV (64W, 365nm)-H ₂ O ₂ (10 mmol)= 88.68% decolorisation, 59.85% degradation. Sunlight-H ₂ O ₂ = 80.15% decolorisation, 50.91% degradation. Dye auxiliaries like Na ₂ CO ₃ , NaOH seriously retard decoloration rate while NaCl does not.	28 (2004)
	O ₃ followed by UV/ H ₂ O ₂	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 ₂₅₄), accelerated subsequent 55 min. H ₂ O ₂ (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).	34 (2001)
	UV /H ₂ O ₂ /O ₃	Wastewater containing disperse dyestuff & pigments	99% COD (Initially 930 mg/l) and 96% color removal in 90 min. [pH=3; H ₂ O ₂ =200 mg/l; O ₃ = 2 g/h; 15 W lamp, 254 nm]. Over 90% removal by UV/O ₃ with less cost due to no requirement of pH adjustment and H ₂ O ₂ .	(2004) 35
	Fe ²⁺ /O ₃	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 ₅ /COD ratio at natural acidic pH of dye bath (3.6 mM Fe ²⁺ , [Fe ²⁺]: [O ₃]= 1:14; FeSO ₄ .7H ₂ O= 1000 mg/l). Negligible TOC removal is due to low O ₃ dose of 14 g/l.	36 (2001)
	UV/Fenton	Disperse ^{NN} red 354	85% color removal (Dye=100 mg/l) & 90% COD removal within 10 mins. with 24.5 mmol H ₂ O ₂ /l and 1.225 mmol FeSO ₄ /l at pH=3, resulting effluent having only 7.29% inhibition in bioluminescence test. Presence of dispersing agent reduces removal efficiency.	37 (2003)
	UV/Fenton	Reactive ^{NN} brilliant red X-3B	Stable decoloration (Dye= 7.7x10 ⁻³ M) within 20 min. with [H ₂ O ₂]= 18x10 ⁻³ M, [Fe ²⁺] or [Fe ³⁺]=1.1x10 ⁻³ M, 75W UV ($\lambda < 320$ nm) lamp. Use of Fe ²⁺ is preferable to Fe ³⁺ because of faster reaction rate with H ₂ O ₂ and evolution of HO ₂ instead of HO ₂ .	38 (2001)
	Solar/Fenton	Orange II (Acid ^{NN} 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 ⁻²) and also by natural sunlight (80 mW cm ⁻²) with 0.92 mM Fe ²⁺ and 10 mM H ₂ O ₂ /hr [pH=2].	39 (1996)
	Solar/Fenton	Monoreactive ^{NN} Procion red H-E7B, Hetero-bireactive ^{NN} Red cibacron FN-R, Standard trichromatic mixture	Sunlight, supplying higher number of photons (3-4x10 ¹⁷ W cm ⁻²) than the low power artificial source (350 nm, 6W, 1.3x10 ¹⁴ W cm ⁻²), 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 ²⁺ and 100-250 mg/l H ₂ O ₂ [pH=3].	40 (2004)
	Cu(II)/Glucic acid/H ₂ O ₂	Direct Chicago sky blue ^{NN} , Methyl orange ^{NN} , Reactive ^{NN} black 5; Poly ^{AQ} B-411, Reactive ^{AQ} blue 2, RBBR ^{AQ} , Acridin (Basic) ^{AQ} orange, Azure blue TH , Crystal violet ^{TPM}	Over 90% decolorization of 100 ppm dye within 24 hr. (70-80% within first 6 hr.) with 10 mM CuSO ₄ , 200 mM H ₂ O ₂ and low dose of glucic acid (15 mM). Insensitive to pH, unlike fenton reaction.	41 (2004)
	UV/ O ₃ /TiO ₂	Textile effluent containing Reactive ^{NN} dye	Removals (60 min.) - Photocatalysis (0.1 g/l anatase TiO ₂ , 125 W, fluency rate 31.1 J m ⁻² s ⁻¹ , pH=11): Color= 90%, TOC= 50%; Ozonation (pH=11, 14 mg/l): Color= 60%, TOC= negligible; Combined: Color=100%, TOC= 60%, Toxicity=50%	42 (2000)
	UV/ H ₂ O ₂ /TiO ₂	Eosin Y ^{XN}	Enhanced decoloration (100% for 50 mg/l dye) & mineralization (95%) in 1 hr (19W lamp, 1g/l TiO ₂ , 100 mg/l H ₂ O ₂ , pH=5.4) along with 85% reduction in toxicity.	43 (2003)
	Solar/ H ₂ O ₂ / Polymeric metalloporphyrins	Acridin (Basic) ^{AQ} orange	% [Decoloration, Degradation]: Hg lamp (450 W, 8hr) Catalysis (3mg/35ml) with H ₂ O ₂ (0.4 g/l) = [87, 92]; without H ₂ O ₂ = [77, 86]. Solar light (3hr) Catalysis without H ₂ O ₂ = [77, 90]. Dye= 13.3 mg/l, high pH favourable.	44 (2002)
	Pulsed streamer corona discharge (electrical)/ H ₂ O ₂	Rhodamine B ^{XN} (Basic), Acid ^{NN} Methyl orange, Direct ^{NN} Chicago sky blue	Pulsed high voltage (20 kV, 25Hz) electrical discharge in water, yielding photo-dissociation of added H ₂ O ₂ (8.8x10 ⁻⁴ mol/l), showed enhanced decoloration rate (100% for 10 mg/l dye in 60 min.) as compared to individual process-performances.	45 (2002)
	Photoelectrochemical	Methylene blue TH	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 ⁻² ; 1gTiO ₂ /200 ml; 30 V DC; Natural pH(6.6)].	46 (2002)
	Microwave (MW)/ Photocatalysis	Rhodamine B ^{XN} (Basic)	In contrast to negligible removal by MW (300W), or less removal by photocatalysis (75W, 0.3mW cm ⁻² ; 30 mg TiO ₂ /30 ml) alone, combined process achieved 97% decoloration (Dye= 0.05 mM) and 73% TOC removal within 3 hrs at pH=5.5.	47 (2002)
	Photoelectrocatalysis	Reactive ^{NN} brilliant orange K-R	Decoloration and TOC removal of dye (0.5 mM) in 0.5 mmol l ⁻¹ NaCl solution within 60 min. (Natural pH): i) Adsorption on packed material: 9%, -; ii) Photocatalysis [TiO ₂ (antase= 70%) coated quartz sand, 500 W high-pressure mercury lamp]: 70%, 20%; iii) Electro-oxidation [30.0 V DC cell voltage, reaction flow rate=190 ml min ⁻¹ , 0.05 MPa airflow]: 77%, 7%; iv) Photoelectrocatalysis: 96%, 38%. Obvious enhancement effect (unlike photocatalysis) of salt in solution.	48 (2003)
	UV/Electro-Fenton	Reactive ^{NN} Red 120	TOC removal [180 min.]: 30%; Decoloration [30 min.]: 75-85% for 60-100 mg/L concentration; Low efficiency due to radical scavenging by the graphite cathode. Detoxification [90 min.]: Safely disposable.	49 (2004)
	Gamma irradiation/ H ₂ O ₂	Reactive ^{TC} blue 15 (Chrozol turquoise blue G), Reactive ^{NN} black 5 (Chrozol black 5)	H ₂ O ₂ 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).	49 (2004)
	Sonolysis/ MnO ₂	Acid ^{NN} red B	Sonication (50 kHz, 150 W) enhanced oxidation property of MnO ₂ (1 g/l) by improving mass transfer, removal of passivating outer oxide layer & production of H ₂ O ₂ , eventually realizing 94.93% decolorization (argon atmosphere) and 48.12 % TOC removal (oxygen atmosphere) [initial pH=3, 240 min.].	50 (2003)
	Sonolysis / Fenton's reaction	Acid ^{NN} Methyl orange	Addition of FeSO ₄ ([Fe ²⁺]= 0.1-0.5 mM) resulted in Fenton's reaction with H ₂ O ₂ 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.	28 (2000)
	Sonolysis/O ₃	C.I Reactive ^{NN} black 5 (RBB)	Combined sonolysis (520 kHz) and ozonation (irradiation intensity, O ₃ input and volume were 1.63 W cm ⁻² ; 50 l/h; and 600 ml) showed synergistic effect, doubling the decolorization (100%, 15 min.) and mineralization (76%, 1hr) rate.	51 (2001)
	Sonolysis/O ₃	Acid ^{NN} 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.	52 (2000)
	Sonolysis/UV /O ₃	C.I Acid ^{NN} orange 7	Enhanced O ₃ (40 g m ⁻³) diffusion by mechanical effects of ultrasound (520 kHz, 600 W) & the photolysis (108W) of ultrasound-generated H ₂ O ₂ to produce .OH led to complete decoloration (Dye= 57µM), 40% TOC removal & an im-	53 (2004)

2. Types

A. Photochemical Process

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, ozone or Fenton's reagent [26] 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 [27] and/or a specifically designed reactor. [54] 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 [29]. Arslan et al [34] proposed pre-ozonation to remove high UV-absorbing components, and thereby accelerate subsequent H₂O₂-UV treatment by increasing UV-penetration. Simultaneous use of UV/H₂O₂/O₃ has also been reported to yield enhanced reaction kinetics. [35] However, this entailed additional cost as compared to UV/H₂O₂ or UV/O₃, and hence such use is recommended to be weighed against degree of removal required and associated cost. As activator of oxidants like O₃ or H₂O₂, handful of studies have put forward other alternatives to UV, namely, reduced transition metals, gamma irradiation [55,56], humic substances 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 TiO₂, ZnO, ZrO₂, CeO₂ etc. or sulfides such as CdS, ZnS etc.) have been used as photo-catalysts so far in different studies. However, titanium dioxide (TiO₂) in the anatase form is the most commonly used photocatalyst, as it has reasonable photoactivity [57]. Moreover it also furnishes the advantages of being insoluble, comparatively inexpensive, non-toxic, together with having resistance to photocorrosion and biological immunity [58]. The photocatalytic process can be carried out by simply using slurry of the fine catalyst particles dispersed in the liquid phase in a reactor or by using supported/ immobilized catalysts. Limitations of slurry reactors are low irradiation efficiency due to the opacity of the slurry, fouling of the surface of the radiation source due to the decomposition of the catalyst particles and 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 O₃ or H₂O₂, exhibiting enhanced decoloration and mineralization, are also available. Considering the total mineralization of the compounds, the photocatalytic ozonation (UV/O₃/TiO₂) may show much lower specific energy consumption than the conventional photocatalysis (UV/TiO₂) and ozonation (UV/H₂O₂/O₃). Fenton reagent (a mixture of H₂O₂ and Fe²⁺) and its modifications such as thermal Fenton process or photo-Fenton reaction using Fe (II)/Fe (III) oxalate ion, H₂O₂ and UV light have received great attention as means for decolorization of synthetic dyes. [59,60] In the case of photo-Fenton technique, H₂O₂ is utilized more rapidly by three simultaneous reactions namely direct Fenton action, photo-reduction of Fe (III) ions to Fe (II) and H₂O₂ photolysis. Thus this process produces more hydroxyl radicals in comparison to the conventional Fenton method or the photolysis. Certain reports suggest that in case of similar removal performance, Fenton's process may be preferred to related

advanced oxidation alternatives (e.g., UV/H₂O₂) in view of lower energy consumption, lower H₂O₂ consumption, lower sludge disposal cost (as compared to higher reagent cost), higher flexibility and lower maintenance requirement [61]. However Fenton reagent necessitates use of a large amount of acidic and alkaline chemicals (ideal pH about 2.5). Compared to Fenton's reagent catalyzed H₂O₂ oxidation process takes advantage of its applicability over a wider pH range between 4 to 8, and moreover no sludge is produced. In order to take advantage of the oxidizing power of Fenton's reagent yet eliminate the separation of iron salts from the solution, the use of 'H₂O₂/ Iron powder' system has been recommended. Such process may yield better dye removal than 'H₂O₂/ Fe²⁺' due to the chemisorption on iron powder in addition to the usual Fenton type reaction. Fenton-type reactions based on other transition metals (e.g., Copper), although less explored to date, have also been reported to be insensitive to pH and effective for degradation of synthetic dyes. [41,62] Among the AOPs, the photo-Fenton reaction and the TiO₂ mediated heterogeneous photocatalytic treatment processes are capable of absorbing near-UV spectral region to initiate radical reactions. Their application would practically eliminate major operating costs when solar radiation is employed instead of artificial UV light. The ferrioxalate solution that has long been being used as chemical actinometer may be used in photo-Fenton process to derive further benefit by replacing UV with solar radiation. Recently, several attempts have been made to increase the photocatalytic efficiency of TiO₂; 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 TiO₂ is only about 3% [63].

B. Electrochemical / Photochemical

In electrochemical treatments, oxidation is achieved by means of electrodes where a determined difference of potential is applied. On this principle, several different processes have been developed as cathodic and anodic processes- direct and indirect electrochemical oxidation, electrocoagulation, electrodialysis, electromembrane processes and electrochemical ion exchange. Occasionally, combination of electrochemical technology and photocatalysis has been adopted to yield some unique advantages. For instance, chemical synergism of photocatalysis and electrochemical processes may yield enhanced decoloration and COD removal and added advantage may be derived from existence of salt in solution, which originally is detrimental for sole photocatalysis. [48] Conversely, electro-Fenton process requires no addition of chemical other than catalytic quantity of Fe²⁺, since H₂O₂ is produced in situ, thereby avoiding transport of this hazardous oxidant. [64,65] In pulsed high voltage electric discharge process, addition of oxidants such as H₂O₂ yields highly reactive free radical species through photo-dissociation of H₂O₂ and thereby enhances the whole process [45].

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 H₂O sonolysis with production of radical species and direct or indirect (via free radicals) destruction of solute. However, stand alone application of sonolysis hardly results in complete mineralization of pollutant streams containing complex mixtures of organic and inorganic compounds. In view of the substantial amount of energy employed in generating free radicals via acoustic cavitation bubbles, efforts have been made to improve its efficiency. It has frequently been explored in association with other AOPs. For example, combined use of sono-photochemical process can prevent severe mass transfer limitation and reduced efficiency of 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 [66,67].

3. Advance Oxidation Process with Physico-Chemical Process

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 [68].

A. Coagulation

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 [23]. In the coagulation process, it is difficult to remove highly water-soluble dyes, and even more important, the process produces a large quantity of sludge. Nevertheless, researchers are persistent in their pursuit of minimizing the limitations of this technology. 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. [69] Multistage application of coagulation followed by ozonation was proved to be superior to their single pass sequential application (total ozonation time the same). The advantage of the multistage application was more convincing in case of wastewater with more recalcitrant composition.

B. Adsorption

Adsorption techniques, specially the excellent adsorption properties of carbon-based supports have been utilized for the decolorization of dyes in the industrial effluents. [70] 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. 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. [71] Adsorption concurrent with ozonation, UV-H₂O₂ or microwave induced oxidation has been reported to yield mutual enhancements like catalysis of AOP by adsorbent and simultaneous regeneration of adsorbent. A rather elaborate method involving solvent extraction and catalytic oxidation has been documented in the literature. [72,73] 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.

C. Membrane Process

Membrane separation endows the options of either concentrating the dyestuffs and auxiliaries and producing purified water [208], or removing the dyestuff and allowing reuse of water along with auxiliary chemicals [74], or even realizing recovery of considerable portion of dye, auxiliaries and water all together. 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. Numerous studies have reported on application of membrane filtration (UF/NF) following coagulation/flocculation to produce reusable water. [75,76] 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. 88 Application of separate technologies for segregated streams has been recommended by different researchers.

4. Biological Treatment Based Combinations

A. Combination among Biological Processes

Conventionally a chemical coagulation step, proceeded by or antecedent to [77] biological treatment, is applied for dye wastewater. Combined treatment with municipal wastewaters is usually favored wherever applicable. A variety of biological treatment processes including activated sludge, fluidized biofilm, different fixed film systems or combinations thereof [78] 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. [26] Toxicity of dye wastewater and factors inhibiting permeation of the dye through the microbial cell membrane reduce the effectiveness of biological degradation. Trials with varieties of combinations including simultaneous anaerobic/ aerobic process (microbial immobilization on a matrix providing oxygen gradient [27] or an anaerobic aerobic hybrid reactor [95]), anoxic plus anaerobic/ aerobic process [79], anaerobic/ oxic system [5], aerobic (cell growth)/ anaerobic (decolorization) system [37] have all been explored involving fed-batch, sequencing batch or continuous feeding strategies with encouraging results. 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 but also because some of these compounds, e.g., azoxy compounds, may cause toxicity. [62] 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.

B. Hybrid technologies based on biological processes

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. 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 physicochemical 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. [60] 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. [43,100] Conversely, enhancement of COD removal (e.g., after ozonation) [80] or improvement of settleability of sludge (e.g., after electrofloatation) [60,62,63,64,65] may require physico-chemical treatment subsequent to AOPs.

2 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. [29] 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. Careful consideration of characteristics of each AOP would facilitate selection of a proper pre-oxidation process for rendering wastewater more amenable to biological treatment. Mantzavinos et al. [81] 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. 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 [82].

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, predominantly activated carbon, have been directly added into the activated sludge systems in certain studies. The fact that the additional removal of soluble organic 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, has persuaded researchers to hypothesize a synergistic relationship between activated carbon and microorganism ('enhanced microbial degradation and bioregeneration of adsorbent'). 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. [78] Although simultaneous adsorption and biodegradation treatment occasionally has been demonstrated as a mere combination of adsorption and biodegradation without any mutual enhancement [72] and has controversies in bioregeneration hypothesis [82], 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. However, in case of oxidative degradation, subsequent substrate adsorption on carbon may plummet. Carbon biocatalyst amalgamation in adsorption cartridges for decoloration has been commercialized ('BIOCOL') in UK [70].

4. Biodegradation/ Membrane filtration

a. Chronological application

For reusable water production, researchers have recurrently referred to nano filtration (or low pressure reverse osmosis) of biologically treated colored wastewater since this option involves less fouling as compared to that for direct nano filtration of dye baths.³³ Some references have put forward inclusion of sand filtration/ multimedia filtration and/or microfiltration in between biological treatment and nanofiltration [83]. Conversely, provision of advanced oxidation of biologically treated wastewater before sending it for nanofiltration has been reported to yield further increased membrane life. [84] 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. Rinsing water may be reused after reclamation by membrane while the concentrated waste may be degraded in anaerobic digester. 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.

5. Membrane bioreactors

Membrane bioreactor (MBR), a remarkable improvement over the conventional activated sludge treatment [85], has been set forth as a promising option in colored wastewater treatment. MBR for decoloration has often been envisioned in conjunction with simultaneous adsorption. 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. [86] For reuse purpose MBRs have occasionally been envisaged as the main treatment process prior to a polishing nanofiltration step [87], or even as the core of a rather elaborate treatment train including anaerobic/ aerobic pretreatment prior to MBR and ozonation following it. [29] 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 [88], loss of the extracellular enzymes and mediators with discharged water, and excessive growth of fungi. 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.

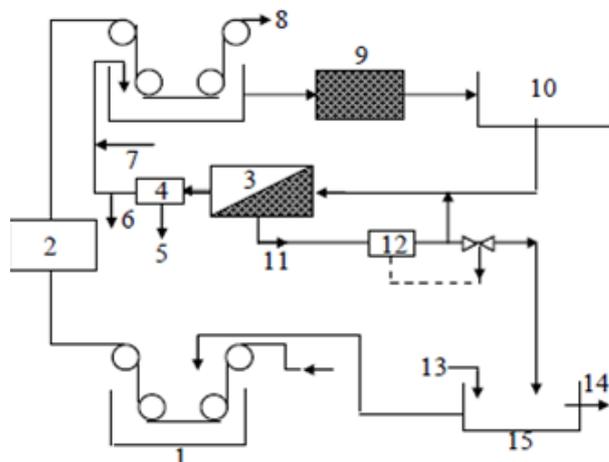
5. Proposed Hybrid Process

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

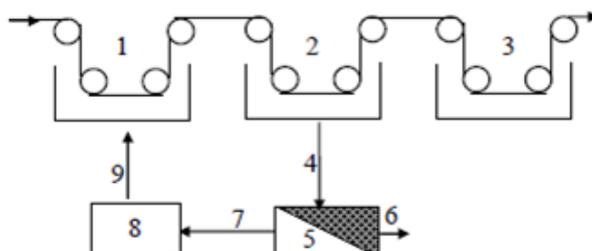
to dyeing and finishing, and, ii) a segregated plant concerning only dyeing and finishing. Additionally, an ideal state of practice of recovery and reuse of textile chemicals (sizing agent, detergent, lanolin from raw wool scouring, caustic for cotton mercerizing, dye bath electrolyte), energy (heat) and water by using appropriate membranes has been assumed (Figure 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. Furthermore, available techno economical 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. 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 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. 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 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 cannot be diluted. Under this condition, the dye bath effluent and rinse water may be directly fed to the MBRAOP sequence, and then desalinated by membrane (RO/NF), with the concentrate (salt) and permeate (water) being reused. 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 MBR189, utilization of concurrent AOP-adsorption system 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

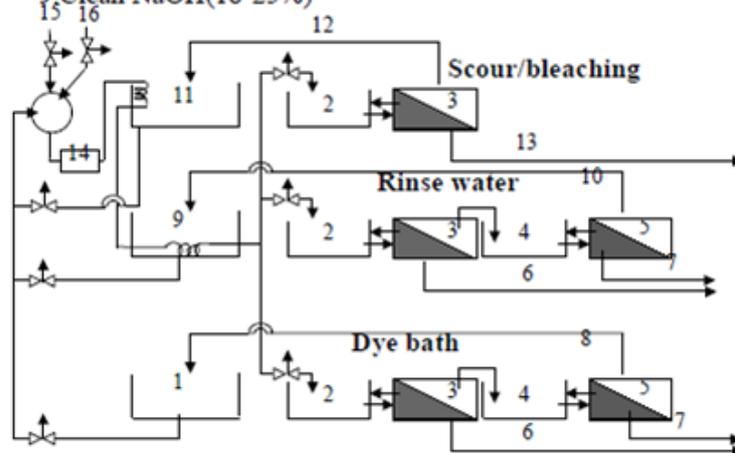
by AOP (may be combination among AOPs themselves) prior to MBR treatment may appear to be more appropriate in near future. Conversely, incineration/ wet air oxidation of dye bath concentrate (possessing high calorific value) remaining after material and water recovery by membrane may also furnish an attractive solution.



PVA recovery: 1.Slasher, 2.Weaving/others, 3.UF membrane, 4.Permeate 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

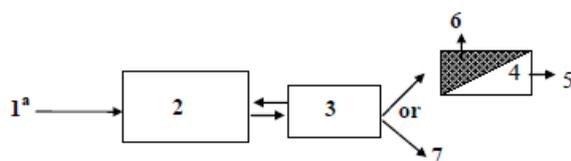


Caustic recovery (Mercerizing): 1.Mercerizing (25% NaOH), 2.Warm water wash, 3.Hot water wash, 4. Contaminated NaOH(6%), 5.Membrane, 6.Concentrate(Fibers, washing agent), 7.Purified NaOH(6%), 8.Evaporator, 9.Clean NaOH(18-25%)



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

Figure 2. Different stages of textile wet processing and associated scopes of material recovery



Integrated MBR-AOP-Membrane treatment scheme
 1.Wastewater^a; 2.Membrane separated fungi reactor; 3.Solar photocatalytic reactor; 4. RO membrane; 5,7.Recyclable water; 6.Concentrated salt

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

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