Chapter 5
Hybrid Treatment Technologies for Dye Degradation in Wastewater

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Abstract Industrial effluents from textile, paper, pharmaceutical and food processing industry are contaminated with high concentration of various dyes. Most of the dyes are aromatic with azo (–N=N–) and nitro ($–NO_2$) functional groups. The effluents containing dyes can affect aquatic life, human health and environment due to toxic, non-biodegradable and carcinogenic nature of dyes. Advanced oxidation processes (AOPs) are known to decolourize and degrade dye effluents. However, a single AOP or any other physicochemical process alone is ineffective for complete degradation of the dye. Therefore, hybrid treatment technologies comprising a combination of AOPs or physicochemical processes have gained recognition in the recent decade for the removal of recalcitrant compounds. In the present chapter, an in-depth evaluation of potential hybrid technologies is performed with a focus on previous literature on hybrid treatment methods for the degradation of dye in wastewater. In addition, limitations of the different hybrid systems are discussed for their better application during wastewater treatment.

Keywords Advanced oxidation processes · Dye wastewater · Hybrid treatment systems · Industrial wastewater treatment · Physicochemical treatment

5.1 Introduction

The rapid industrialization in the recent years has contaminated of one of the most essential natural resource—water. The increased volume of wastewater and pollution levels in natural water bodies have resulted water shortage in many parts of the world. Industries such as textile, leather dyeing, paper printing, cosmetic, pharmaceutical and food processing generate wastewater with high chemical oxygen demand (COD) and strong colour due to the presence of dyes and other chemicals (Khataee et al. 2012). Textile effluents have strong colour, high pH, suspended solids, organics,

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Table 5.1 Typical wastewater characteristic of textile industry effluents

Parameters	Values						
	Aydiner et al. (2019)	GilPavas et al. (2019)	Zazou et al. (2019)	Geraldino et al. (2020)	Silva et al. (2020)	Lebron et al. (2021)	Louhichi et al. (2022)
pH	6.2	9.1	8.75	5.7	7.9	7.7	6.8
Temperature (°C)	25.4	n.a	22	27.5	n.a	n.a	20.2
Colour (mg Pt-Co/L)	n.a	1366	n.a	1715	134	n.a	n.a
COD (mg/L)	2830	875	267	656	65	1771	713
BOD (mg/L)	n.a	190	n.a	158	n.a	n.a	n.a
Electric conductivity (mS/cm)	2.6	12.8	2.5	1.4	2.3	3.8	8.6

n.a. not assessed

metals and salts (Shindhal et al. 2020). The typical wastewater characteristics of a textile industry wastewater from recent literature are summarized in Table 5.1. The wastewater composition depends on the process, equipment, fabric, dye and season.

The dyes can be characterized based on their origin as natural and synthetic dyes. The synthetic dyes are further classified based on their mode of application (such as reactive, direct, disperse, basic and vat dyeing) and according to their chemical structure or functional group (i.e., azo, anthraquinone, sulphur, triarylmethane and phthalocyanine (Yaseen and Scholz 2019). Chromophore groups such as azo (–N=N–), nitro (–N=O), carbonyl (–C=O) quinoid and auxochrome groups (e.g., amine, carboxyl, sulphonate and hydroxyl) in the dye structure impart colour to the dye (Holkar et al. 2016).

Dye containing wastewater can pollute the nearby water bodies and are a serious threat to human health and aquatic life due to the toxic and carcinogenic nature of dyes. The colour of wastewater is aesthetically unpleasant and it can affect the oxygen solubility in water bodies (Gupta et al. 2015). The recalcitrant nature of dye makes it resistant to the conventional biological treatment processes. Hence, it is essential to treat dye containing effluents prior to their discharge into aquatic systems.

Literature suggests that the application of a single process may not be sufficient for the complete degradation of mixtures of dye in wastewater. Therefore, there is a growing interest in hybrid treatment technologies comprising a combination of AOPs or physicochemical processes for effective dye degradation. However, hybrid treatment methods must be evaluated for their application at large scale. The present chapter provides an overview of various existing technologies and emerging hybrid technologies for the degradation of dye in wastewater. In addition, the limitations and challenges of hybrid treatment methods are also discussed. Further, recommendations are provided for future research work in this area.

5.2 Advanced Treatment Technologies

Advanced oxidation processes (AOPs) offer a viable treatment option for treatment of refractory wastewaters having low biodegradability. They have been found to be effective for the degradation and mineralization of recalcitrant organic compounds (Oturan and Aaron 2014). AOPs are based on in situ production of highly reactive and unselective hydroxyl radicals. AOPs can be broadly classified into Fenton-type, ozone based, irradiation based, electrical, ultrasonic and thermal processes. These processes can be carried out in the presence or absence of catalysts in homogenous or heterogeneous medium. An overview of various AOPs is present in Fig. 5.1.

The selection of an AOP is dependent on the wastewater characteristics, cost effectiveness and environmental compliances which have to be met for any location. A few AOPs such as ozonation and photolysis are already well established for wastewater treatment at large scale (Miklos et al. 2018). However, many of the other AOPs must be evaluated for their performance at industrial scale. In this section, the process and reactions of the most widely used AOPs are briefly discussed. In addition, the previous literature on the degradation of dyes by the selected AOPs are also summarized.

5.2.1 Fenton-Type Processes

The traditional Fenton's oxidation process involves the formation of highly reactive hydroxyl radical ($OH^{\cdot}$) in presence of Fenton's reagent i.e., a combination of

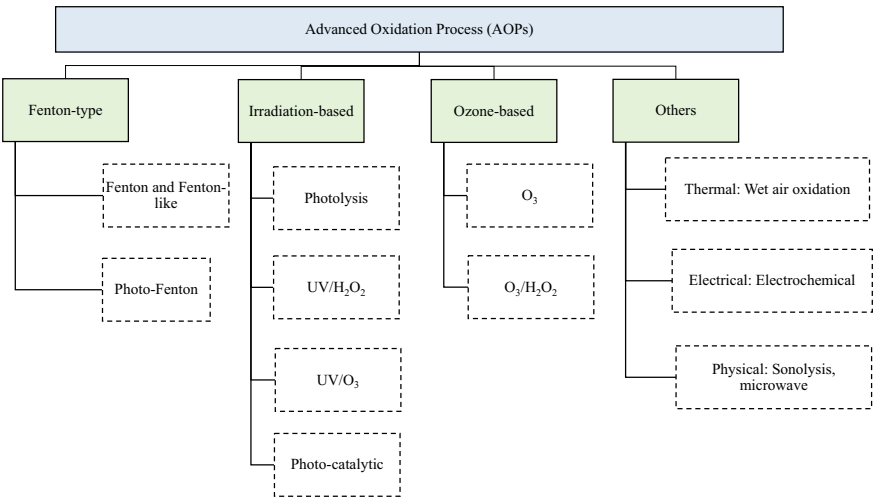

Fig. 5.1 Classification of advanced oxidation processes for wastewater treatment

hydrogen peroxide and ferrous ions in homogenous system (Babuponnusami and Muthukumar 2014). Hydroxyl and sulphate radicals can be generated from H_2O_2 and $S_2O_8^{2-}$, respectively in the presence of ferrous ions as per Eqs. 5.1 and 5.2 (Walling 1975). The redox potentials of hydroxyl ($OH^{\cdot}$) and sulphate ($SO4^{-\cdot}$) radicals are 2.8 eV and 2.5–3.1 eV, respectively (Anandan et al. 2020). The generated $OH^{\cdot}$ radical can abstract the hydrogen from organic compounds to produce organic radical ($R^{\cdot}$) as per Eq. 5.3.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \tag{5.1}$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Fe^{3+} \tag{5.2}$$

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \tag{5.3}$$

Fenton's oxidation has been used previously for the treatment of a mixture of four reactive dyes (i.e., remazol black 5, remazol red, remazol yellow 84 and remazol brilliant blue) having total initial dye concentration of 300 mg/L by Meriç et al. (2003). The reaction pH, temperature, $FeSO_4$ concentration and H_2O_2 dose were 4, 50 °C, 500 mg/L and 1000 mg/L, respectively. Under the above mentioned conditions, a COD removal of 93% and colour removal of >99% could be achieved. In contrast, heterogeneous Fenton-like oxidation was carried out using scrap zero-valent iron for textile industry wastewater having initial COD of 875 mg/L (GilPavas et al. 2019). A colour removal of 95% and COD removal of 76% was obtained at initial pH of 3 with 2 g/L catalyst and 24.5 mM H_2O_2 dose after 1 h duration. An advantage of Fenton's process is that it can be performed at room temperature and the reagents used during the process are readily available (Silva et al. 2020). To further increase the efficiency of the process, variation of Fenton's such are electro-Fenton, photo-Fenton, sono-Fenton and Fenton-like processes have been explored.

5.2.2 Irradiation Based Processes

Photolysis oxidation is carried out in the presence of a light source (UV, visible or LED). The presence of UV irradiation to the oxidants such as hydrogen peroxide or persulphate can enhance their degradation to form hydroxyl ($OH^{\cdot}$) and sulphate ($SO_4^{\cdot -}$) radicals as per Eqs. 5.4 and 5.5 (Samsami et al. 2020).

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\cdot} \tag{5.4}$$

$$S_2O_8^{2-} + h\nu \rightarrow SO_4^{\cdot -} \tag{5.5}$$

In past, photo-oxidation (UV/H_2O_2) of a mixture of dyes (CI basic red 46, malachite green and CI basic blue) showed a colour removal of 97% by Khataee et al. (2012). The optimum condition for initial concentration of dyes, H_2O_2 dose and reaction time were 4 mg/L, 48 mg/L and 30 min, respectively as determined from central composite design.

The photocatalytic degradation using semiconductors as catalysts involves the adsorption of light or photon having energy greater than bandgap of the semiconductor material forming electron–hole pairs which can result in formation of hydroxyl radicals as per Eqs. 5.6 and 5.7 (Miklos et al. 2018; Dhangar and Kumar 2020).

$$TiO_2 + hv \rightarrow \left(e^- + h^+\right) \tag{5.6}$$

$$h^+ + {OH^-}_{ad} \rightarrow {}^{\cdot}OH_{ad} \tag{5.7}$$

Semiconductor materials like TiO_2 and ZnO have been widely used as a catalyst due to their higher efficiency under UV irradiation in the last few decades. Juang et al. (2010) performed the photocatalytic oxidation of acid orange 7 and reactive red 2 having initial concentration of 0.086 mM each under UV/TiO_2 system. The authors have reported complete removal of dyes with 0.5 g/L TiO_2 dose after 20 min of reaction.

Photo-Fenton process is a modification of traditional Fenton's process where light energy (UV or solar) is coupled with Fenton's reagent. Complete decolourization of a mixture of dyes (remazol red RR and remazol blue RB) could be achieved in 2 h during homogeneous photo-Fenton oxidation at an initial reaction pH of 3 (Punzi et al. 2012). The initial concentration of each dye was 50 mg/L with 0.25 mM iron and 12 mM H_2O_2 dose. Photocatalytic processes have the advantages of higher efficiencies without the formation of sludge. However, the efficiency of photocatalytic process depends on the availability of photon, intensity of light, reaction pH, presence of oxidants and catalysts (Oturan and Aaron 2014).

5.2.3 Ozone Based Processes

Ozone is an unstable gas which can react directly as molecular ozone or through secondary oxidants i.e., hydroxyl radicals. The reaction of ozone with organic compound can be represented by Eq. 5.8 which suggests that for every three moles of ozone, two moles of $OH^{\cdot}$ radical are generated (Malik et al. 2020).

$$3O_3 + OH^- + H^+ \rightarrow 2OH^{\cdot} + 4O_2 \tag{5.8}$$

The chain termination occurs in the presence of carbonates, bicarbonates and hydroperoxyl radical (Eqs. 5.9–5.11).

$$OH^{\cdot} + CO_3^{2-} \rightarrow CO_3^{\cdot -} + OH^{-} \quad (5.9)$$

$$OH^{\cdot} + HCO_3^{-} \rightarrow HCO_3^{\cdot} + OH^{-} \quad (5.10)$$

$$OH^{\cdot} + OH_2^{\cdot} \rightarrow O_2 + H_2O \quad (5.11)$$

Ozonation has been used effectively for the selective degradation of organic pollutants having double bonds (e.g., C=C) and functional groups (e.g., $–CH_3$, –OH). Previously, wastewater containing sirius blue dye (initial concentration = 400 mg/L) showed 91% colour removal with ozone dose of 24.03 g/m^3 by Turhan and Turgut (2009). Ozonation can be carried out at room temperature and pressure with no sludge production (Dhangar and Kumar 2020). Therefore, it considered a cleaner process for the treatment of high strength wastewater.

5.2.4 Other AOPs

Electrochemical processes have been used widely for water and wastewater treatment. The effect of different electrode materials, oxidants and experimental conditions for a variety of pollutant has been reviewed by Chen (2004). These processes are not affected by the presence of salts or ions in the wastewater. Electrochemical oxidation of synthetic wastewater comprising sixteen dyes (total initial dye concentration = 361 mg/L, initial COD = 281 mg/L) using titanium-tantalum-platinum-iridium (Ti–Ta–Pt–Ir) anode and stainless steel cathode showed more than 95% decolourization within 15 min (Chatzisymeon et al. 2006). The initial reaction pH, electrolyte and current were 7.5, NaCl (0.5%) and 5 A, respectively.

Sonolytic processes are AOPs which use ultrasound wave for the degradation of organic contaminants. Ultrasound waves have frequencies ranging higher than the hearing range of humans i.e., 20 kHz to 10 MHz (Pirsaheb and Moradi 2021). Cavitation is process of formation, growth and implosion of bubble or cavities under ultrasound waves producing high pressures and temperatures in the microsystem (Gągol et al. 2018). The ultrasound waves are transmitted by acoustic cavitation where highly reactive radicals are generated as per Eq. 5.12. The hydrogen radical produced converts into hydroperoxyl radical in the presence of oxygen which later forms hydrogen peroxide as per Eqs. 5.13 and 5.14 (Anandan et al. 2020).

$$H_2O + \text{ultrasound})))) \rightarrow OH^{\cdot} + H^{\cdot} \quad (5.12)$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \quad (5.13)$$

$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (5.14)$$

Recently, sonocatalytic oxidation of methyl orange (initial concentration = 20 mg/L) was performed at 42 kHz ultrasound frequency in the presence of Au/Fe_3O_4 nanoparticles as catalysts (de Jesús Ruíz-Baltazar 2021). A removal of 92% was observed during the process with catalyst dose of 0.075 g/L. Sonolysis process can be operated at ambient conditions without the use of any chemicals. They are considered safer and cleaner processes that are not affected by the toxicity or biodegradability of the pollutant (Chakma and Moholkar 2016; Pirsaheb and Moradi 2021). Therefore, it is widely combined with other treatment techniques for enhanced removals. The advanced oxidative treatment options for dye removal are summarized in Table 5.2.

Table 5.2 Degradation of dyes using advanced oxidation processes

Process	Wastewater characteristics	Results	References
Fenton's oxidation	Total concentration of dye mixture = 300 mg/L	COD removal = 93%; colour removal = >99%	Meriç et al. (2003)
Fenton-like oxidation	Initial COD of textile industry wastewater = 875 mg/L	COD removal = 76%; colour removal = 95% in 1 h	GilPavas et al. (2019)
UV/H_2O_2	Concentration of dye mixture (CI basic red 46, malachite green and CI basic blue) = 12 mg/L	Colour removal = 97% in 30 min	Khataee et al. (2012)
Photo-Fenton process	Concentration of dye mixture (remazol red RR and remazol blue RB) = 100 mg/L	Colour removal = 100% in 2 h	Punzi et al. (2012)
UV/TiO_2	Concentration of dye (acid orange 7 and reactive red 2) = 0.086 mM	Dye removal = 100% in 20 min	Juang et al. (2010)
Ozonation	Concentration of dye (sirius blue) = 400 mg/L	Colour removal = 91%	Turhan and Turgut (2009)
Electrochemical oxidation	Total concentration of dyes = 361 mg/L, initial COD = 281 mg/L	Colour removal = 95% in 15 min	Chatzisymeon et al. (2006)
Sonocatalytic oxidation	Initial methyl orange concentration = 20 mg/L	Dye removal = 92%	de Jesús Ruíz-Baltazar (2021)

5.3 Limitations of AOPs

AOPs have shown promising results for the degradation of a variety of dyes as reviewed in the previous section. The various advantages of individual AOPs are summarized in Table 5.3. Despite the high efficiencies of AOPs, the application of these processes are limited due to various reasons. In this section, the drawbacks and limitations of different AOPs will be briefly discussed.

Fenton's oxidation processes are effective in the pH range of 2–4 and therefore, acidification of initial wastewater and neutralization of treated wastewater is required. High oxidant and iron dosage are required for higher degree of oxidation increasing the cost of the process (Babuponnusami and Muthukumar 2014). Fenton's and electrochemical process generate sludge during the process which must be disposed-off appropriately (Hai et al. 2007).

Photocatalytic processes are efficient in UV light but the efficiency is low under visible light. At higher doses of the catalyst, scattering is observed which further reduces the efficiency of the process (Zainal et al. 2007). Another drawback of this process is the difficulty in separation of catalysts from the aqueous solution. To

Table 5.3 Advantages and limitations of various advanced oxidation processes

Process	Advantages	Limitation	References
Fenton's process	• Simple and easy operation • High pressure or temperature is not required	• Effective in acidic pH • Formation of sludge • Neutralization is required	Babuponnusami and Muthukumar (2014)
Photocatalytic process	• No sludge is produced • High COD removal	• Catalyst separation and reuse is difficult • High operational cost due to lamps • Light scattering at higher catalyst doses	Zainal et al. (2007)
Ozone based processes	• No sludge is produced • No chemicals are used	• High energy and operational cost due to ozonators	Dhangar and Kumar (2020)
Electrochemical process	• Effective in COD reduction • Presence of salts do not affect the process	• Generation of sludge • High electricity cost	Hai et al. (2007)
Cavitation process	• Effective oxidation of hydrophilic and hydrophobic organics • Lower mass transfer limitation • Low operational cost as compared to other AOPs	• Difficult to achieve optimum ultrasonic frequency • Efficiency reduces for larger volumes (>10 L)	Gągol et al. (2018)

improve the efficiency in visible light doping with metal or non-metal can be done while a solid support material can be used to easily separate the catalyst.

The selective nature of ozone limits the mass transfer and wide application of the process. The sonochemical method do not produce secondary pollutants but they require long duration for complete degradation of pollutant. The removal efficiencies have been found to reduce with increase in the volume of wastewater during cavitation process (Gągol et al. 2018). The advantages and limitation of various AOPs are compiled and presented in Table 5.3.

Most of the AOPs such as photocatalytic, electro-oxidation, ozonation and sonication process are energy intensive and highly operational and maintenance costs is associated with these processes. To reduce the cost of the process without affecting its efficiency, combination of various processes can be explored.

5.4 Emerging Hybrid Treatment Technologies

The limitations of the individual AOPs suggest that a standalone AOP is not sufficient and efficient for the treatment of complex dye containing wastewater streams. It is therefore necessary to understand the potential of the combination of different techniques for the effective wastewater treatment of industrial effluents.

In this subsection, hybrid processes involving photocatalytic processes are divided into two types for easier understanding. The first combination is photochemical methods coupled with electrochemical methods while the second combination is photochemical methods coupled with sonolytic methods. Other combinations such as ozonation coupled with cavitation and sonication coupled with Fenton process have also been used for dye degradation. However, in this section, previous literature on (i) electro-photocatalytic and (ii) sono-photocatalytic hybrid process for degradation of dyes has been discussed in details.

5.4.1 Photochemical Processes Coupled with Electrochemical Processes

A combined process using electrochemistry and photochemistry has gained popularity in the last few decades. Photo-electrocatalytic degradation of turquoise blue 15 (initial concentration = 0.025 mM) dye was carried out by using Ti/TiO_2 photoanode and Pt cathode under UV light (125 W) by Osugi et al. (2005). The authors reported complete decolourization and 95% mineralization at an initial pH of 2 in 6 h duration. Similarly, electrochemical assisted photo-degradation of six dyes (i.e., methyl orange, naphthol blue black, reactive blue 2, methylene blue, rhodamine 6G and direct red 81) having total initial dye concentration of 1000 mg/L was carried out by Zainal et al. (2007). A COD removal of 73% could be obtained for the dye

mixtures after 150 min of the combined treatment with TiO_2/Ti plate anode and platinum cathode under light irradiation (wavelength = 360–830 nm). In another study, photo-electro-Fenton process was combined with heterogeneous photocatalytic process using TiO_2 nanoparticles immobilized on glass plates for the treatment of CI basic red 46 dye (Khataee et al. 2011). Colour removal of 89% could be obtained in 35 min by the combined photo-electro-Fenton/UV/TiO_2 process where ferric concentration, initial dye concentration and current were 0.1 mM, 15 mg/L and 300 mA, respectively. The colour removal reported by authors for the individual AOPs i.e., UV/TiO_2, electro-Fenton and photo-electro-Fenton were 12, 32 and 84%, respectively suggesting higher efficiency of the combined treatment process.

On the other hand, Almeida et al. (2014) coupled photo-electro-catalytic process with electro-Fenton process using Pt/TiO_2 nanotubes photoanode and PTFE cathode for the degradation of acid red 29 dye (initial concentration = 85 mg/L)). A total organic carbon (TOC) removal of 98% could be obtained in the combined system (current density = 16.6 mA/cm^2, Hg lamp = 80 W) at initial pH of 3 in the presence of ferrous ions (0.5 mM) after 2 h duration. The authors suggest that the addition of TiO_2 nanotubes with Pt nanoparticles decreases the band gap energy and increases the degradation efficiency due to adsorption in visible region. Conversely, photo-electro-Fenton has also been combined with photocatalytic process for the removal of CI basic red 46 dye (initial concentration = 20 mg/L) by Zarei et al. (2010). The photocatalyst used in this study was TiO_2 while carbon nanotube-PTFE were used as cathode and Pt sheet was used as anode. A TOC removal of 99% was achieved in 6 h using the combined process (initial pH = 3, current = 100 mA and Fe^{3+} = 0.1 mM) while 92% decolourization could be observed within 1 h duration. A summary of previous literature on electrochemical processes coupled with other AOPs is presented in Table 5.4.

5.4.2 *Photochemical Processes Coupled with Sonolytic Processes*

The integration of sonolysis with photocatalysis (i.e., sonophotocatalysis) works on the synergistic effects of generation of radical and electron–hole pairs at high temperature and pressure. Advantages of sonophotocatalysis include improved light penetration, uniform distribution of catalysts, reduced mass transfer limitations, regeneration of catalyst surface and higher radical production (Pirsaheb and Moradi 2021).

TiO_2 has been used as a catalyst for sonophotocatalytic oxidation of methyl orange (initial concentration = 100 μM) under xenon-arc lamp (450 W) in ultrasonic bath (213 kHz) (He et al. 2011). Complete mineralization was observed at an initial pH of 2 with 1 g/L TiO_2 dose in 120 min. Sathishkumar et al. (2014) performed sonophotocatalytic oxidation of acid blue 113 (initial concentration = 0.01 mM) with Y^{3+} doped TiO_2 (catalyst dose = 1 g/L) catalyst in the presence of visible light

Table 5.4 Summary of hybrid electrochemical processes for dye degradation

Wastewater characteristics	Reaction conditions	Results	References
Initial concentration of turquoise blue 15 = 0.025 mM	Anode = Ti/TiO_2, cathode = Pt, initial pH = 2	Colour removal = 95% in 6 h	Osugi et al. (2005)
Total initial dye concentration = 1000 mg/L	Anode = TiO_2/Ti plate, Cathode = Pt	COD removal of 73% in 150 min	Zainal et al. (2007)
Initial concentration of CI basic red 46 dye = 20 mg/L	Anode = Pt sheet, cathode = carbon nanotube-PTFE, initial pH = 3, current = 100 Ma, Fe^{3+} = 0.1 mM	TOC removal = 99% in 6 h	Zarei et al. (2010)
Initial concentration of CI basic red 46 = 15 mg/L	ferric concentration = 0.1 mM, current = 300 mA	Colour removal of 89% could be obtained in 35 min	Khataee et al. (2011)
Initial concentration of acid red 29 dye = 85 mg/L	Anode = Pt/TiO_2 nanotubes, cathode = PTFE, current density = 16.6 mA/cm^2, initial pH = 3, ferrous ions = 0.5 mM	TOC removal = 98% in 2 h	Almeida et al. (2014)

and ultrasound (42 kHz). The authors have reported 65% mineralization after 5 h duration.

ZnO was used a photocatalyst for the oxidation of direct blue 71 (initial concentration = 100 mg/L) in an ultrasonic bath (20 kHz) under UV light (Ertugay and Acar 2014). The sonophotocatalytic processes resulted in complete colour removal in 20 min with 1 g/L ZnO and 75 mg/L H_2O_2 at an initial pH of 2.5. In another study, acid blue 113 degradation was carried out using zinc oxide catalysts (dose = 0.88 g/L) and persulphate as oxidant (dose = 2.43 mM) under UV light (9 W) at ultrasound frequency of 20 kHz. A removal efficiency of 98% was reported by authors at an initial pH of 6.1 in 25 min (Asgari et al. 2020).

Authors have also studied sono-photo-ferrioxalate system for the decolourization of acid red B dye (initial concentration = 20 mg/L) under UV irradiation (160 W) at ultrasound frequency of 40 kHz (Chakma and Moholkar 2016). The decolourization obtained during the process was 85% after 60 min at reaction pH of 3 with Fe^{3+}/oxalate ratio of 1:3. A summary of previous literature on electrochemical processes coupled with other AOPs is presented in Table 5.5.

Table 5.5 Summary of hybrid sono-photochemical processes for dye degradation

Wastewater characteristics	Reaction conditions	Results	References
Initial concentration of methyl orange = 100 μM	Ultrasound frequency = 213 kHz, initial pH = 2, TiO_2 dose = 1 g/L	Dye removal = 100% in 2 h	He et al. (2011)
Initial concentration of acid blue 113 = 0.01 mM	Ultrasound frequency = 42 kHz, Y^{3+} doped TiO_2 dose = 1 g/L	TOC removal = 65% in 5 h	Sathishkumar et al. (2014)
Initial concentration of direct blue 71 = 100 mg/L	Ultrasound frequency = 20 kHz, ZnO dose = 1 g/L, H_2O_2 = 75 mg/L, initial pH = 2.5	Colour removal = 100% in 20 min	Ertugay and Acar (2014)
Initial concentration of acid red B dye = 20 mg/L ()	Ultrasound frequency of 40 kHz, Fe^{3+}/oxalate = 1:3, initial pH = 3	Colour removal = 85% in 1 h	Chakma and Moholkar (2016)
Initial concentration of acid blue 113 = 200 mg/L	Ultrasound frequency = 20 kHz, ZnO dose = 0.88 g/L, persulphate = 2.43 mM, initial pH = 6.1	Dye removal = 98% in 25 min	Asgari et al. (2020)

5.5 Conclusions and Future Prospects

The discharge of coloured effluent containing dye into the natural waterbodies not only results in aesthetic pollution but it also affects aquatic life. The effective treatment of dye wastewater is a challenge due to their recalcitrant nature and carcinogenic properties. Several AOPs have been found effective for the degradation of dye wastewater and a few have been implemented at large scale. However, AOPs are bound to certain practical limitations for industrial application. Moreover, AOPs have high energy demand and operational costs making them expensive for industrial use. To overcome the shortcomings of individual AOPs, hybrid treatment processes have been found efficient for the removal of dyes in wastewaters by various researcher. The present chapter summarizes state-of-art information on hybrid treatment technologies derived from integration of AOPs. Among the various hybrid techniques, sono-photocatalysis have attracted the attention of most scholars. The advantage of sono-photocatalysis process has reduced mass transfer limitations due to increased turbulence and regeneration of catalyst surface. However, the selection of an appropriate hybrid technology will be case-specific depending on the initial wastewater characteristic and end-use of the treated effluent. Further, efforts are required for their industrial application in future. A few recommendations regarding the research on hybrid process are as follows:

- The potential of hybrid treatment technologies needs to evaluated for industrial effluents by piloting these technologies.

- A detailed discussion on the kinetics of the hybrid process must be performed for better understanding.
- Studies should be performed to find a cost effective and environmental friendly treatment option by utilizing solar energy and waste materials.

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