CHAPTER 2

Literature Review

CHAPTER 2

Nowadays, textile dyes emission become a serious environmental issue imposing detrimental effects on human health and ecosystems. The toxic and persistent textile dyes need a sustainable and innovative remediation technique. Various remediation techniques are critically reviewed in the following subsections.

2.1 Textile Wastewater Treatment Techniques

The direct or indirect exposure of textile effluents into our environment pose severe hazards. Therefore, it is essential to adopt a suitable, economically viable, and environmentally friendly technique for the complete mineralization of textile effluents. Meanwhile, various treatment techniques are available for textile wastewater treatment, comprised of numerous physiochemical (such as adsorption/biosorption, coagulation and flocculation, photochemical oxidation, electrochemical oxidation, ozonation, and membrane filtration) and biological processes (that adhere biotic agents like bacteria, fungi, algae, and plants) (Kumar et al., 2021).

2.1.1 Physiochemical Techniques

Adsorption, membrane-based separation techniques, and ion exchange are the most popular physical treatment techniques, whereas electrochemical, coagulation/flocculation, and oxidation techniques are chemical methods. Adsorption, a surface-based phenomenon, solid adsorbent (such as activated carbon, charcoal, silica gel, alumina, and zeolite) attract adsorbate molecules/ions (from polluted water) to its surface. Carbon-based adsorbents such as activated carbon, charcoal, and biochar have traditionally been using, even though activated carbon has lots of importance at the industrial level. This method allows the mass transfer of pollutants from one phase into another and does not mineralize the pollutant. Membrane-based separation technique (membrane filtration), size exclusion method, selectively permeate solute molecule

through its pores. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are extensively in use for textile dye color removal, salinity, and COD reduction. The ion exchange process has applications in heavy metal removal, water purification, and textile effluents treatment. Ion exchange resins have their functional groups charge on them, charged dyes also have a unique charge, the ionic attraction between resin and charge dye molecule makes a strong bond, deposits dye on the surface of the resin, color removal occurs.

Chemical techniques (exemption for electrochemical technology) are relatively more expensive with physical and biological methods. The dye removal via this technique requires proper equipment as well as a large number of chemicals and electrical energy, the secondary waste generates from it is toxic and creates waste disposal problems, restrict its wide range of process applicability. Electrocoagulation (EC) tank consists of two metal electrodes, a direct current source, and in-situ formed coagulant particles. Electrolytic reduction and oxidation take place, anode made up of metal acts as a catalyst as well as a coagulant reagent. An overall, the reactor generates odorless and colorless water. Other advantages are no additional chemical requirement, no secondary waste generation, economically viable, and environmentally friendly. Electro-Fenton (EF), integration of electrolysis and Fenton's reaction, removes organic wastes through the process combination of coagulation and oxidation. Recently, advanced oxidation processes (AOPs) are especially used for wastewater treatment. In another process, called coagulation-flocculation, chemical coagulants such as aluminium sulfate solution ($Al_2(SO_4)_3.18H_2O$) inject under vigorous mixing conditions. Neutralization of oppositely charged dispersed particles happens, flocculants thereby add, a conglomeration of fine particles forms a larger particle. The sedimentation process allows the removal of these particles.

2.1.1.1 Advanced oxidation processes (AOPs)

Advanced Oxidation Processes (AOPs) are a group of innovative techniques used in wastewater treatment to remove persistent organic pollutants and contaminants that are difficult to degrade using conventional methods. AOPs involve the generation of highly reactive hydroxyl radicals (•OH) or other powerful oxidants to break down and oxidize organic compounds into simpler, less harmful substances (Feijoo et al., 2023). Hydroxyl radicals have a high oxidation potential (2.80 V) and can react with a wide range of contaminants, including pharmaceuticals, pesticides, dyes, and emerging contaminants (ECs). These reactions typically involve the transfer of an electron from the contaminant to the hydroxyl radical, resulting in the degradation of the pollutant into smaller, more biodegradable molecules. Various oxidizing agents are generated during a typical oxidation process having enough oxidation potential, as illustrated in **Figure 2.1**.

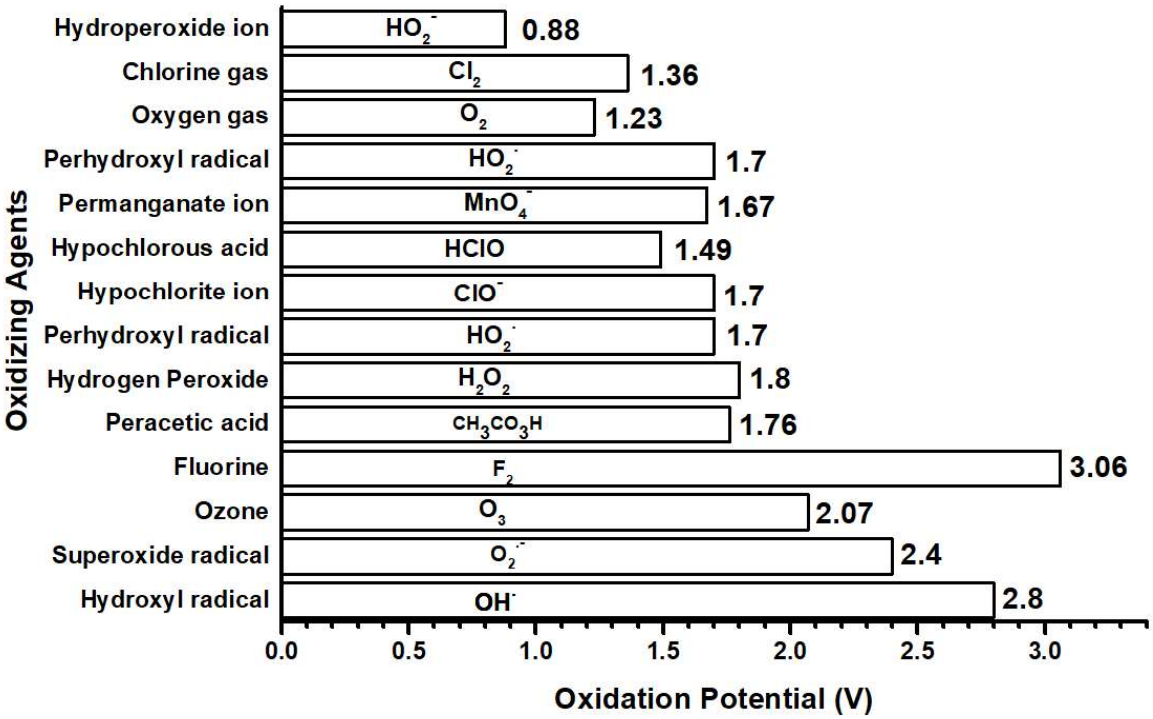

Figure 2.1. An illustration of various oxidizing agents generated during the advanced oxidation process along with respective oxidation potential

The efficiency and effectiveness of AOPs depend on several factors, such as the type of oxidants used, reaction conditions, and the presence of catalysts or energy sources. Various AOPs have been developed and employed in wastewater treatment, including methods such as Ozonation, Fenton's reagent (a combination of Hydrogen Peroxide and Ferrous Iron), Photocatalysis, and Non-Thermal Plasma (Bilińska and Gmurek, 2021; Hafeez et al., 2021; Junploy et al., 2021; Liu et al., 2021). Each technique has its own unique mechanisms for generating hydroxyl radicals or other powerful oxidants, providing flexibility and adaptability to different wastewater compositions and treatment requirements. These processes are known for their versatility and efficiency in treating complex wastewater streams and have gained significant attention in recent years due to their potential to address emerging environmental challenges. AOPs offer enhanced treatment efficiency, flexibility in handling different wastewater compositions, and the potential for on-site treatment applications. These advanced techniques play a vital role in addressing the growing challenges of water pollution and ensuring the availability of clean and safe water resources.

2.1.1.1.1 Photocatalysis

Photocatalysis is an innovative, sustainable advanced oxidation technique that utilizes light energy and a catalyst to degrade and remove organic pollutants in wastewater. Specifically, photocatalysis involves the use of a photocatalyst, typically a semiconductor material such as Titanium (IV) oxide (TiO_2), which absorbs UV light energy and creates electron-hole pairs. These photo-induced electron-hole pairs undergo redox reactions with water and oxygen present in the surrounding environment, generating highly reactive species such as hydroxyl radicals (HO•), superoxide radicals ($O_2^{\cdot -}$), and holes (h^+) that can oxidize and degrade organic pollutants (Junploy et al., 2021). The photocatalytic process effectively degrades a wide range of pollutants, including dyes, pesticides, pharmaceuticals, and organic contaminants.

The photocatalytic oxidation mechanism can be summarized as given below (Tiwari et al., 2022):

Photoexcitation: $TiO_2 + h\nu$ (UV irradiation) $\rightarrow TiO_2$ (e^- (CB) + h^+ (VB))

Ionization of water: H_2O (ads) + h^+ (VB) $\rightarrow$ OH• (ads) + H^+ (ads)

Ionosorption of Oxygen and superoxide radical generation: $O_2 + e^-$ (CB) $\rightarrow O_2^{-\bullet}$ (ads)

Superoxide protonation and formation of hydroperoxyl radical (HO_2•):

$O_2^{-\bullet}$ (ads) + $H^+ \leftrightarrow HOO^\bullet$ (ads)

$2HOO^\bullet$ (ads) $\rightarrow H_2O_2$ (ads) + O_2

H_2O_2 (ads) $\rightarrow$ 2OH• (ads)

Organic Pollutants + OH• $\rightarrow CO_2 + H_2O$ (Formation of intermediate compounds)

Organic Pollutants + h^+ (VB) $\rightarrow$ Oxidized Product

Organic Pollutants + e^- (CB) $\rightarrow$ Reduced Product

Some commonly used Photocatalyst along with their energy band gap are illustrated in **Figure 2.2**.

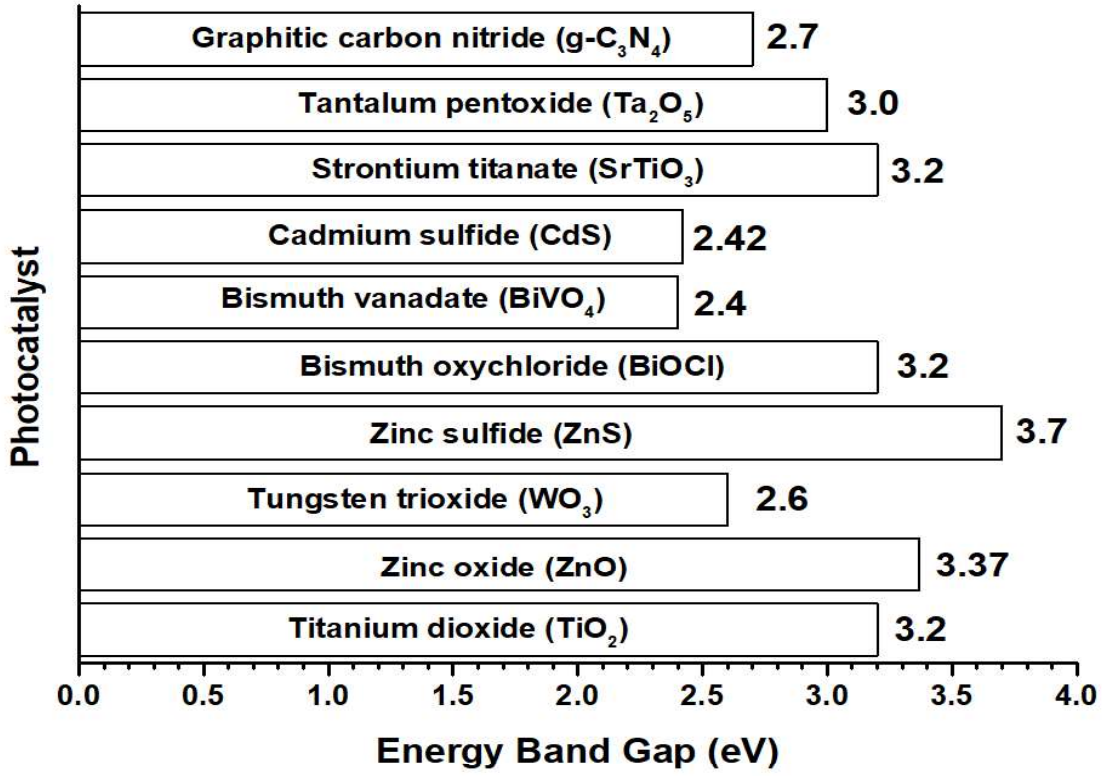

Figure 2.2. A typical illustration of various semiconductor-based photocatalysts along with their energy band gaps

Furthermore, photocatalysis operates under mild reaction conditions, typically at room temperature and ambient pressure. This not only reduces energy consumption but also minimizes the formation of unwanted by-products or secondary pollutants. Additionally, photocatalytic systems can be easily integrated into existing wastewater treatment processes, providing a cost-effective solution for improving overall treatment efficiency. Another advantage of photocatalysis is its ability to degrade pollutants directly in aqueous solutions, eliminating the need for additional chemical reagents or the production of excessive sludge. This makes it a cleaner and more environmentally friendly approach to wastewater treatment (Al-Mamun et al., 2019).

Moreover, photocatalytic systems can be coupled with other treatment technologies, such as biological processes, to enhance the overall treatment performance (Samsami et al., 2020). By

combining different techniques, synergistic effects can be achieved, resulting in improved pollutant removal efficiency and water quality. Therefore, photocatalysis is a promising technology for wastewater treatment due to its effectiveness in degrading organic pollutants, mild operating conditions, the potential for mineralization, and utilization of renewable energy sources (Dihom et al., 2022). Its environmentally friendly nature, versatility, and potential for integration with existing treatment processes make it an attractive option for sustainable and effective water purification.

2.1.2 Biological Techniques

As a matter of custom, the biological process overwhelmingly gains widespread application for the treatment of industrial textile wastewater. Bacteria, fungi, algae, and yeast play a vital role during a typical biodegradation process of organic pollutants. Because bacterial culture is grown (cultured) easily, having high specific growth rates, and possesses enough potential towards the mineralization of recalcitrant organic compounds, and so is abundantly used for dye degradation (Yang et al., 2014). The bioremediation technique uses biotic agents (bacteria, algae, fungi, etc.); to stimulate their culture growth under a dye-stress environment with the addition of nutrients (Mishra and Maiti, 2020). Nutrients are responsible for microbial growth and promote their activity, and efficiently the mineralization of dye occurs (Rasool and Lee, 2016). Microorganisms presents in contaminated sites have more affinity towards waste mineralization and are allowed for immobilization/entrapment within solid support, leading to partial or complete mineralization/transformation of the dye molecule. Glucose, fructose, sucrose, yeast extract, molasses, and seed powder are used as co-substrates, provide the nutritional source for microorganisms, and act as electron donors to break the chemical bond present in the dye molecule (Spennati et al., 2020). Aerobic or anaerobic microorganisms are used abundantly for the remediation of organic waste on a large scale (Mallikarjuna and Dash, 2020). In the anaerobic process, mineralization occurs in the absence of oxygen and converts

organic matter into biogas, whereas the aerobic process utilizes oxygen as an electron acceptor to convert organic matter into simple end products (Ji et al., 2020). The cleavage of high molecular weight, complex organic molecules occurs through successive steps, also known as metabolic pathways. As the mineralization proceeds, energy liberation takes place and simultaneously has consumed by the microorganisms to stimulate their growth (Sur and Mukhopadhyay, 2018).

2.2 Biodegradation of Textile Dyes

The biodegradation of textile dyes depicts the interaction between the metabolic capabilities of microorganisms and the complex chemical structure of dyes. Microorganisms such as bacteria, fungi, yeast, and algae break down and metabolize the complex dye compounds present in textile wastewater, convert them into less harmful and simpler substances (Varjani et al., 2020). They possess numerous enzymatic systems and metabolic capabilities; facilitate the degradation of various textile dyes. However, degradation pathway could vary and mostly depending on the specific microbial species and dye structure.

Bacterial species comprise *Alcaligenes faecalis* (Hossen et al., 2019), *Bacillus megaterium* KY848339.1 (Ewida et al., 2019), *Acinetobacter baumannii* JC359 (Ameenudeen et al., 2021), *Micrococcus yunnanensis* (Carolin et al., 2021), *Bacillus pseudomycoides* (Kumar et al., 2019), *Bacillus stratosphericus* SCA1007 (Akansha et al., 2019), *Acinetobacter baumannii* (Unnikrishnan et al., 2018), and *Staphylococcus* sp. K2204 (Velayutham et al., 2017) can degrade textile dyes. Reactive Red-22, an azo dye with an initial concentration of 200 mg/L, was completely decolourized by *Escherichia coli* NO3 (Chang and Kuo, 2000). The decolourization rate increased under the temperature range (20-45 °C), and neutral or basic pH (7-9) enhanced the decolourization activity. An isolated photosynthetic bacterium *Rhodopseudomonas palustris* W1 exhibited 95% decolourization of Reactive Black-5 (RB5) dye with an initial concentration of 700 mg/L in the presence of light with additional nutrient

supplement including lactate or glutamine (carbon source; more than 500 mg/L concentration of lactate), ammonium chloride (nitrogen source; more than 100 mg/L), NaCl (5 wt%) (Xingzu et al., 2008). The author reported that RB5 reduction led to the formation of partial aromatic amines, which subsequently further degraded as the reaction period extended. Anthraquinone dyes have complex aromatic structures, recalcitrant towards microbial degradation (Mishra and Maiti, 2018). Reactive Brilliant Blue (KN-R) decolorization was studied under anaerobic conditions through an isolated bacterial strain *Rhodocyclus gelatinosus* (XL-1) and achieved 93% decolorization efficiency in the presence of peptone (Dong et al., 2003). The co-metabolism was liable for the decolourization at a temperature of 30 °C and pH 7. In another study, the decolourization of vat red-10 dye (0.01%) occurred under aerobic conditions through the synergistic effect of *Galactomyces geotrichum* MTCC 1360 and *Pseudomonas desmolyticum* NCIM2112 (Gurav et al., 2011). The author found 2,6-di-isopropyl naphthalene as the end product with 55.5% degradation within 23 days under the oxidative metabolic process. Solvent Green (SG) (10 mg/L) degradation was studied by *Hortaea* sp. and complete decolorization occurred within 24 h, laccase and 1.2-dioxygenase enzymes were responsible for the biodegradation (Al Farraj et al., 2019). Triphenylmethane dyes are characterized by their molecular structure, which consists of a central carbon atom (methine group) bonded to three phenyl groups (aromatic rings). In this regard, various actinobacteria isolated from soil were examined for the degradation of Malachite green (MG), Methyl violet (MV), Crystal violet (CV), and Cotton blue (CB) dyes (Adenan et al., 2020). The author reported that species of *Streptomyces*, *Kitasatospora*, *Rhodococcus*, and *Nocardiopsis* exhibited decolorizing efficiency. Among them, *N. alba* showed the highest degradation efficiency of 97.0%, 95.1%, 95.8%, and 83.8% for MG, MV, CV, and CB, respectively, within 14 days. The incorporation of bacterial consortia improves the degradation efficiency through their combined effect. A comprehensive analysis of bacterial consortia for dye degradation is illustrated in **Table 2.1**.

Table 2.1 A comprehensive analysis of various textile dye degradation using bacterial consortium.

S.N.	Dye	Bacterial Consortium	Process Parameters	Dye Removal %	References
1.	Congo red, Ranocid Fast Blue, Bordeaux, and Blue BCC	SKBII, *Bacillus vallismortis*, *Bacillus cereus*, *Bacillus megaterium*, *Bacillus pumilus*, and *Bacillus subtilis*	Dye Concentration: 10–100 mg L^{-1}, Temperature: 37 °C	50–60%	(Tony et al., 2009)
2.	Red HE3B	*Providencia* sp. SDS and *Pseudomonas aeuroginosa* BCH	Dye Concentration: 50 mg/L, Process time: 1 h	100%	(Phugare et al., 2011)
3.	Rubine GFL	*Brevibacillus laterosporus* MTCC 2298 and *Galactomyces geotrichum* MTCC 1360	Dye Concentration: 50 mg/L, 30 h incubation	100%	(Waghmode et al., 2012)
4.	Blue Bezaktiv S-GLD 150	Lyophilised bacterial consortium	Dye Concentration: 1 g/L dye loading:15 g dye/m^3·d	88–97%	(Khouni et al., 2012)
5.	Acid orange 7	Sewage sludge mixed aerobic culture	Dye concentration: 100 mg/L;	99% color and 66% COD removal	(García-Martínez et al., 2015)
6.	Reactive green-19	*Bacillus pumilus* HKG212 and *Zobellella taiwanensis* AT 1–3	Optimum Conditions: pH, 8.3, Temperature, 32.04 °C, Yeast extract, 1.16g/100 mL	97%	(Das and Mishra, 2017)
7.	Remazol Brilliant Violet 5R (RBV-5R)	*Hydrogenophaga* spp. and *Georgenia* sp.	Sulfate reduction efficiency is 70%. The COD/sulfate ratio is 2. Permeate alkalinity is 2588 ± 222 mg/L $CaCO_3$	86% COD removal, 99.5%. dye removal	(Yurtsever et al., 2017)

8.	Novacron Super Black G, Novacron Orange FN-R, and Bezema Yellow S8-G	*Vibrio* sp., *Bacillus* sp., and *Neisseria* sp.	6 days static incubation, Temperature: 37 °C, and each dye concentration: 100 mg/L	Bezema Yellow S8-G (65%), and Novacron Super Black G and Novacron Brilliant Blue FN-R (90%)	(Karim et al., 2018)
9.	Sudan I	*Shewanella putrefaciens* CN32 and *Bacillus circulans* BWL1061	pH:8, NaCl amount: 0-20 g/L, Temperature: 26 °C	90.23%	(W. Liu et al., 2018)
10.	Reactive Red 198	*Klebsiella variicola* and *Enterococcus faecalis*	Initial Concentration: 10-25 mg/L, Bacterial concentration: 3.5 mL × 10^5 cells/mL, 72 h incubation	More than 98% dye removal	(Eslami et al., 2019)
11.	Reactive Red 239	Activated sludge is inoculated; *Aliivibrio fischeri* is used as the test organism for toxicity evaluation	Dye concentration: 50 mg/L, Ozone dose: 40 and 20 mg/L	95% color removal 91% COD, 81% DOC, and 79% NH_4^+ removal efficiency	(Dias et al., 2019)
12.	Disperse Red 3B	*Aspergillus* sp. XJ-2 and *Chlorella sorokiniana* XJK	Dye Concentration: 0.1 g/ L, Temperature: 25 °C, 96 h incubation	98.09% color removal and 93.9% COD reduction	(Tang et al., 2019)
13.	Real textile 6.wastewater	*Aspergillus carbonarius M333* and *Penicillium glabrum* Pg1	Color: 400 ± 15.5 Pt-Co, 3 days incubation	78.8% color removal and	(Arikan et al., 2019)

				67.7% COD removal	
14.	Novacron Super Black G	*Bacillus sp.* AZ28, *Alcaligenes faecalis* AZ26, and *Bacillus cereus* AZ27	Static condition; Dye Concentration: 200 mg/L, pH:8, Temperature: 37 °C, 96 h incubation	90%	(Hossen et al., 2019)
15.	Methanil Yellow G	*Clostridiisalibacter*, *Marinobacter*, and *Halomonas*	10% salinity, pH:10.0, Dye Concentration: 100 mg/L,	93.3%	(Guo et al., 2020)
16.	Reactive Yellow 145	*Thiosphaera pantotropha* ATCC 35512 and *Pseudomonas aeruginosa* (RS1)	Shaking incubation of 96 h, Dye concentration: 50 mg/L	65%	(Garg et al., 2020)
17.	Direct blue 15, Direct red 23, and Direct yellow 12	Ligninolytic bacterial consortia	Dye concentration: 200 mg/L, 4 days incubation	84% decolorization, 89% COD removal	(Thiruppathi et al., 2021)
18.	Indanthrene Blue RS	*Pseudomonas aeruginosa* NCH (PA), *Bacillus fexus* TS8 (BF), and *Proteus mirabilis* PMS (PM)	loading rate: 100 and 300 mg L^{-1}	90%	(Mohanty and Kumar, 2021)

2.2.1 Major limitations in bacterial-mediated dye degradation

Bacterial-mediated dye degradation offers a promising approach for textile wastewater treatment, but there are certain limitations, too. The narrow substrate specificity of bacteria, as may only be capable of degrading specific types of dyes (Pandey et al., 2007). This restricts their effectiveness in treating a wide range of dye pollutants. It often concentrates on the decolorization of dyes, resulting in the transformation of colored compounds into colorless or less colored intermediates. However, complete mineralization and degradation of the dye molecules into non-toxic end products can be more challenging and may require additional treatment steps. Additionally, the presence of co-substrates or additional nutrients supports the growth and metabolic activity of the bacteria (Castro et al., 2020). Limited availability or imbalance of these co-substrates in the wastewater can hinder the degradation efficiency. However, the degradation of complex and recalcitrant dyes is a time-consuming process (Su et al., 2016). It often requires an extended incubation period to achieve significant degradation. This slow degradation kinetics can pose challenges when dealing with high volumes of wastewater requiring rapid treatment.

2.3 Hybrid Techniques for Textile Dye Degradation

The incorporation of hybrid techniques for the degradation of complex dye from textile wastewater has emerged as an innovative approach to mitigate the limitations, and simultaneously enhance the efficacy of bacterial-mediated degradation processes. It facilitates the effective treatment of a wide range of dye pollutants, comprising recalcitrant and complex dyes, by exploiting the unique capabilities of different techniques. Various process technologies have been studied as hybrid technologies for textile wastewater treatment. Recently, advanced oxidation processes (AOPs) in combination with biological techniques have emerged and are capable of completely mineralizing complex dyes. These include Ozonation, UV-based processes, Ultrasound, Electrochemical Oxidation, Fenton, Photo-

Fenton, Plasma, and Photocatalysis (Samsami et al., 2020). AOPs involve the generation of highly reactive hydroxyl radicals (•OH) or other powerful oxidants to break down and oxidize organic compounds into simpler, less harmful substances (Feijoo et al., 2023). Hydroxyl radicals have a high oxidation potential (2.80 V) and can react with a wide range of contaminants, including pharmaceuticals, pesticides, dyes, and emerging contaminants (Chaturvedi et al., 2022). These reactions typically involve the transfer of an electron from the contaminant to the hydroxyl radical, resulting in the degradation of the pollutant into smaller, more biodegradable molecules. Among AOPs, the photocatalytic oxidation process has been popularly employed for the treatment of various recalcitrant textile dyes. A critical review has been highlighted for the versatility of photocatalytic oxidation towards the treatment of textile wastewater in the following subsection.

2.3.1 Photocatalytic Oxidation

There are various photocatalysts including Zinc Oxide (ZnO), Tungsten Trioxide (WO_3), Strontium Titanate ($SrTiO_3$), Cadmium Sulfide (CdS), Graphitic Carbon Nitride (g-C_3N_4), Tantalum Pentoxide (Ta_2O_5), Bismuth Vanadate ($BiVO_4$), Bismuth Oxychloride (BiOCl), and Titanium (IV) Oxide (TiO_2) have been reported for photocatalytic processes (Jo and Tayade, 2014). Among them, TiO_2 is prominently used due to its several features including high photocatalytic activity, chemical stability, low cost, biocompatible and environmentally safe, good photostability, non-toxicity, wide bandgap (3.2 eV), and commercial availability makes it a preferred photocatalyst (Saqib et al., 2016). Several studies have been reported in the literature on the photocatalytic oxidation of textile dyes. In this direction, So and coworkers demonstrated the photocatalytic oxidation of Procion Red MX-5B dye and reported 90% mineralization within 80 min (So et al., 2002). The optimum conditions were dye concentration: 40 mg/L, UV irradiation intensity: 17 mW/cm^2, TiO_2 concentration: 500 mg/L, pH: 5, and H_2O_2 amount: 10 mM. Further, Muruganandham and Swaminathan (2006) studied

the photocatalytic oxidation of Reactive Yellow 14 dye with TiO_2 under UV-A irradiation (365 nm) and reported that direct photolysis had minimal impact on dye degradation. The optimum conditions were: 4g/L of TiO_2-P25, 32 W of radiation intensity, 15 mM H_2O_2 initial concentration, and 3 g/L of both $KBrO_3$ and $(NH_4)_2S_2O_8$. The decolorization efficiency of TiO_2 and TiO_2-P25 were 57.4% and 91.3%, respectively. Bansal et al. (2010) identified the reaction pathway and intermediates of Acid Orange 7 dye using liquid chromatography-mass spectrometry (LC-MS) and ion chromatography (IC) using TiO_2 in the presence of UV light source. Preliminary batch studies were carried out to investigate the effect of various parameters viz. 0.5-2 g/L photocatalyst loading, 2-10 pH, and 5-100 mg/L initial dye concentration and achieved almost complete decolorization. Polar and sulfonated intermediates were identified using LC-MS, whereas IC gave the presence of NO_3^- and SO_4^{2-} ions, respectively. Gupta et al. (2012) investigated the Amaranth dye photocatalytic degradation in TiO_2/UV system with 100 minutes of UV illumination achieving a maximum decolorization rate of 64%. The combination of UV light, TiO_2 catalyst, and H_2O_2 showed the highest decolorization rate. Sharma and coworkers investigated the photocatalytic oxidation and mineralization of Reactive Black 5 dye using TiO_2 degussa P25 in a slurry reactor with an artificial light source (Sharma et al., 2012). A maximum adsorption capacity of 26.5 mg/g was found at pH 3 with an optimum amount of 1.5 g/L photocatalyst and 70% TOC reduction (100 mg/L dye) obtained after 12 hr of exposure. Furthermore, the photocatalytic decolorization of Reactive Black 5 dye under UV-A light emitting diodes (375 nm) in a continuous stirred tank reactor exhibited a maximum of 89% decolorization (Ferreira et al., 2016). The optimal parameters included 50 mg/L dye concentration, 40 W/m^2 irradiation intensity, 1 g/L TiO_2 dose, and the feed flow rate of 0.8 mL/min, respectively. UV-A LED/TiO_2 demonstrated an effective decolorization with an electrical energy per order of 220 kWh/m^2, flow rate of 4.8×10^{-6} m^3/h, and electric power consumption of 0.0129 kW. Similarly, Abdellah et al.

(2018) employed a slurry reactor for the photocatalytic degradation of methylene blue-containing wastewater using commercial TiO_2 as a photocatalyst. Air sparging was introduced in micro-bubbles form, which in turn improved the degradation efficiency and also elevated the rate of mass transfer. The author found that an air superficial velocity of 2 cm/s, pH of 7, and photocatalyst loading of 1 g/L led to the complete decolorization of 10 mg/L dye solution.

2.3.2 Integration of Photocatalytic Oxidation with Bioremediation

A novel approach to treating dyeing wastewater involves integrating photocatalysis and biodegradation. Although there are limited studies available in the literature. In a study conducted by Brosillon et al. (2008), a combination of photocatalysis and biodegradation was employed for the degradation of Reactive Yellow 145, an azo dye. The researchers observed a decrease in the total organic carbon (TOC) content of the by-products generated from photocatalysis when subjected to subsequent biological treatment using *Pseudomonas fluorescens*. This finding confirmed the viability of integrating photocatalysis with biodegradation, highlighting its potential for effective wastewater treatment. Similarly, Gebregiorgis et al. (2018) employed a combined photocatalysis and biodegradation approach to treating real textile wastewater and achieved complete degradation as well as efficient removal of chemical oxygen demand (COD). Moreover, the addition of hydrogen peroxide enhanced pollutant decomposition by increasing the production of hydroxyl radicals, thereby accelerating the treatment process. Therefore, the integrated photocatalytic oxidation with biodegradation approach demonstrates significant improvement in biodegradability, paving the way for enhanced and sustainable treatment of complex organic pollutants.

The “synergistic effect” (Zhang et al., 2021) of photocatalysis and biodegradation has been categorized into two ways viz. (1) intimate coupling of photocatalysis and biodegradation (ICPB) and (2) independent sequence of photocatalysis and biodegradation (ISPB) (Lu et al.,

2022). ICPB facilitates photocatalysis and biodegradation simultaneously within a single reactor, hence leading to the intimidating mineralization of photocatalysis intermediates and the vanishing of the accumulation of the toxic byproducts (Yu et al., 2020). It not only improves the biodegradability of pollutants but also serves as an enhancement in the treatment efficiency and shortens the process duration. While ISPB incorporates photocatalysis and biodegradation in separate sequential reactors (Deveci et al., 2016). Recalcitrant compounds are preliminary treated in a photoreactor, resulting in oxidized products that are then fed into the bioreactor. The post-biodegradation of photocatalytic oxidized products plays multiple crucial roles, comprising the complete degradation of residual recalcitrant parent compounds to reduce the toxicity of the treated effluents and efficaciously improve the quality (Chebli et al., 2010). Acid red 183 containing textile wastewater was treated using ISPB and achieved 75% COD reduction and 98% dye removal after 10 h (Chebli et al., 2011). The degradation pathway involved the initial cleavage of the azo bond, followed by the oxidation through reactive oxygen species (ROS) or biodegradation. Meanwhile, fewer studies have focused on the ICPB approach, whereas ISPB has been vividly incorporated into textile dyes. For this direction, a TiO_2-coated biofilm carrier was designed for the mineralization of reactive black 5 dye in ICPB, achieving 65% COD reduction and 97% dye removal (Li et al., 2012a). However, the high dye concentration in the ICPB system faces difficulty, imposing a burden on microbes as the dye molecules compete for photons with the photocatalyst, thereby efficiently retarded (Li et al., 2012b; Lin et al., 2011). As a consequence, for high dye concentrations, ISPB exhibits effectively treating the textile wastewater (Lu et al., 2022). A comprehensive process analysis of ISPB has been summarized in **Table 2.2**.

Table 2.2 A comparative performance study of independent sequence of photocatalysis and biodegradation (ISPB) for various textile dye degradation.

S.N.	Dye	Photocatalyst	Biocatalyst	Dye Concentration (mg/L)	Process Performance (% dye removal)	References
1.	Reactive Black 5	TiO_2	Yeast *Candida tropicalis* JKS2	200	74.9	(Jafari et al., 2012)
2.	Crystal Violet	TiO_2	Microbial Consortium	200	76	(Chen et al., 2013)
3.	Ethyl Violet	TiO_2	Microbial Consortium	50	85	(Chen et al., 2014)
4.	Methyl Red	ZnO	*Brevibaccilus laterosporus* and *Galactomyces geotrichum*	500	Complete decolorization within 4 hr but toxicity and COD reduction were low	(Waghmode et al., 2019)
5.	Gardenia-yellow	TiO_2 was doped with $K_2S_2O_8$,	Microbial Consortium	382.4 ± 8.2 mg/L initial COD	COD < 50 mg/L 87.8 % COD reduction	(He et al., 2020)
6.	Reactive Black 5	TiO_2	*Providencia rettgeri*	1250.5 mg/L initial COD,	93.3% dye removal, 90.4% COD reduction	(Ambaye and Hagos, 2020)

2.4 Review on Graphene-Related Compounds for Textile Dye Degradation

Nowadays, graphene-related compounds have emerged as an advanced treatment technology for an efficient and sustainable way to mitigate the severe environmental impact caused by the emission of textile wastewater (Xiao et al., 2020). Due to their unique mechanical, physical, and chemical properties graphene and its derivative compounds such as graphene oxide (GO) and reduced graphene oxide (rGO) are tremendously incorporated for numerous applications comprising biosensors, aerospace applications, fuel cells, energy storage devices, biomedical devices, electromagnetic shielding, and wastewater treatment (Thakur and Kandasubramanian, 2019). GO, aromatic lattices of graphene sheets, have oxygen-containing functional groups such as alcohols, epoxides, carboxylic groups, and ketone carbonyls grafted onto the edge and the basal planes of graphene, liable for their high chemical versatility (Shen et al., 2018). These functional groups are liable for the enhanced dispersibility of GO in various solvents, moreover, provide active sites for chemical reactions, promote catalytic activity, and facilitate interaction with target compounds (Shen et al., 2018). In the context of textile wastewater remediation, due to their adsorption capabilities and catalytic activity towards dye molecules, GO-based materials have shown promising results (Obayomi et al., 2022). The leading application of graphene-derived compounds in the form of hydrogel matrix as an efficient adsorbent is critically reviewed in the following subsections.

2.4.1 Application of GO-Hydrogel Beads for Textile wastewater treatment

Hydrogel beads have three-dimensional structures, and hydrophilic polymer networks, possess high water content, elastic and soft, and can swell in the presence of moisture. Graphene oxide and reduced graphene oxide-based hydrogel beads are popularly used as an adsorbent for the removal of textile dyes efficiently. In this direction, a calcium alginate immobilized graphene oxide (GO/CA) composite was prepared, and investigated its adsorption behavior towards methylene blue dye (Li et al., 2013). The adsorption capacity of GO/CA composite was 140.80

mg/g with an initial dye concentration of 80 mg/L, under the identical conditions GO exhibited an adsorption capacity of 135.44 mg/g. Further, Sui et al. (2013) elucidated the amaranth dye adsorption via the three-dimensional GO-polyethylenimine porous materials and achieved an adsorption capacity of 800 mg/g, also suggested its suitability for CO_2 adsorption (11.2 wt %). Moreover, a mechanically strong hydrogel was synthesized using the free-radical polymerization of sodium alginate (SA) and acrylamide in the presence of GO, abbreviated as GO/SA/polyacrylamide (GO/SA/PAM) ternary composite, and exhibited excellent adsorption behavior towards anionic as well as for cationic dyes (Fan et al., 2013). Similarly, Wang et al. (2014) utilized a one-step approach for the preparation of poly(diallyldimethylammonium chloride)/GO (PDDA/GO) hydrogels and assessed their adsorptive removal with 86.25% removal efficiency for both Trypan Blue (TB) and Ponceau S (PS) dyes at room temperature. The addition of GO not only enhanced the adsorptive behavior towards textile dyes but was also liable for the creation of a porous alginate gel matrix. Acridine orange was adsorbed by macroporous alginic beads, prepared by calcium alginate incorporation and GO was immobilized onto it, found that GO promoted the porosity of beads due to its excellent entrapment (Sun and Fugetsu, 2014). The author reported the adsorption capacity of dye was 4.5 mmol/g with an equilibrium time of nearly 125 min, which was superior to all adsorbents without GO content. Furthermore, Gan et al. (2015) studied the adsorption of methyl blue and methyl orange dye using the GO-filled konjac glucomannan (KGM) hydrogel in which calcium oxide was used as a cross-linker. The presence of GO enhanced the adsorption performance and also decreased the swelling ratio compared to KGM hydrogel. Guo et al. (2015) synthesized GO/polyethylenimine (GO/PEI) hydrogels for the adsorption of methylene blue and rhodamine B dye. PEI was responsible for gelation while GO sheets were reasonably able for the adsorption of the dyes within the hydrogel matrix. Both the dyes achieved 100% removal within approximately 4 h, emphasizing that GO/PEI hydrogels were efficient

adsorbents. A slight modification was proposed for the preparation of GO along with alginate/ polyvinyl alcohol (PVA) hydrogel double network through a facile freeze/thaw method followed by Ca^{2+} crosslinking for the efficient adsorption of methylene blue dye (C. Liu et al., 2018). A maximum of 480.76 mg/g methylene blue dye was adsorbed onto the GO- reinforced SA/PVA hydrogel. Gan and coworkers assessed the removal of bisphenol A and various organic dyes using GO/SA hydrogel beads (Gan et al., 2018). The author found that GO incorporation decreased the pore size and swelling ratio and enhanced the adsorption capacities of organic dyes comprising indigo dye, azo dye, heterocyclic dye, and anthraquinone. Now, the freeze-drying technique was introduced for the preparation of GO and SA-based hydrogel beads along with the combination of crosslinking with $CaCl_2$ (Liu et al., 2019). The author reported that hydrogel beads exhibited a maximum adsorption capacity of 357.14 mg/g for the adsorption of methylene blue dye according to the Langmuir isotherm.

2.4.2 Immobilization of Microorganisms within the Hydrogel Matrix

The entrapment and/or immobilization of microorganisms within the alginate and GO-based hydrogel matrix stimulate their activity and stability. Alginate supports microorganism growth and keeps its structural integrity, whereas a high surface area has provided by the GO sheets. This entrapment technique recently emerge for the mineralization of organic waste. Bacteria-induced GO hydrogel (BGH) was incorporated for the decolorization of congo red dye and bioreduction of Cr (VI) (Shen et al., 2018). The author found that *Shewanella* sp. was responsible for the reduction of GO and led to the formation of three dimensional porous bio-rGO-hydrogel, embedded with extracellular polymeric substance (EPS), rGO, and live bacteria. BGH was formed through stacking, bridging, rolling, and rGO sheets crosslinking mechanisms due to the combined effect of EPS and activities from *Shewanella* sp. *Shewanella xiamenensis* BC01-BGH was able to decolorize 99% congo red dye with a decolorization rate of 201 $mg\,h^{-1}\,g\ cell^{-1}$. Furthermore, bacterial species of *Shewanella xiamenensis* were

subjected to entrapment within the reduced graphene oxide hydrogel network to investigate the synergistic effect (i.e. adsorption and biodegradation) for the treatment of congo red and methylene blue dye (Shen et al., 2019). The hydrogel network depicted the decolorization efficiencies of 99.8% and 97.3% for congo red and methylene blue dye within 55 h, respectively. π–π interaction, electrostatic interaction, and chemical interaction along with immobilized live bacterial species were responsible for the mineralization of these dyes. To understand the interaction between bacterial cells with graphene materials, a facile synthesis was developed for biographene hydrogel, where the bacterial strain of *Shewanella* was entrapped and suggested its suitability for the treatment of textile industry wastewater (Xu et al., 2020). The author reported that a single layer of GO (> 0.30 μm^2) was biocompatible. The self-assembly of GO and *Shewanella* was driven by a combination of different forces, including hydrophobic attraction, electrostatic repulsion, and adhesion force. Moreover, the fabrication of a novel biological graphene aerogel (BGA) using bacteria in waste-activated sludge (AS) as a cross-linker and an ionic dye as a surface charge modification reagent resulted in an aerogel with a porous elastic structure and low density (D. Wang et al., 2020). The presence of packed bacteria within reduced graphene oxide (rGO) sheets enhanced the adsorption capacity of the aerogel. Loading the negatively charged dye (MO) further increased the adsorption capacity by 1.24-fold compared to the unmodified AS-BGA, indicating the effective surface charge modification and improved dye adsorption capabilities of the novel BGA.

2.5 Summary of the Literature and Research Gap

It has long been known that the textile industry generates a massive amount of synthetic waste across the globe. Dye-containing wastewater is carcinogenic, mutagenic, recalcitrant, and xenobiotic. It is essential to make an ecological balance between the consumption of freshwater and efficaciously treating textile wastewater. Textile wastewater treatment techniques aim to eliminate and degrade the pollutants from the wastewater emitted by the textile industries.

These techniques typically comprise physical, chemical, and biological processes to effectively treat wastewater. Physical processes such as sedimentation, filtration, and membrane separation are used to separate solid particles and suspended matter from the wastewater. They simply transfer pollutants from one phase to another and do not mineralize them. Chemical processes like coagulation, flocculation, and advanced oxidation are employed to facilitate the precipitation and removal of dissolved contaminants. Biological processes, such as aerobic or anaerobic treatment, utilize microorganisms to degrade organic pollutants through biochemical reactions.

Biological processes, however effective for the treatment of textile dyes, have suffered certain process limitations. Longer bioprocess time, sensitivity towards environmental conditions, and face inefficacy towards entire mineralization of toxic recalcitrant complex dyes. Meanwhile, the high concentration of complex dyes, which have low biodegradability, can inhibit microbial activity and slow down dye degradation. To overcome these limitations, a hybrid technique combining photocatalysis and biodegradation has emerged as a promising solution. The integration of photocatalysis and biodegradation offers several benefits. Photocatalysis can initiate the degradation of recalcitrant complex dyes, breaking them down into smaller, more readily biodegradable compounds. This enhances the efficiency of the subsequent biodegradation process. Additionally, photocatalysis can target specific pollutants, including recalcitrant compounds and toxic intermediates, which may be challenging for biological processes alone. The combination of both techniques ensures the complete degradation and detoxification of contaminants, resulting in improved wastewater treatment performance. Graphene and graphene oxide (GO)-based hydrogels provide unique features for textile wastewater treatment. Graphene exhibits excellent adsorption capacity and high surface area, enabling effective pollutant removal. GO, with its abundant oxygen-containing functional groups, enhances the adsorption and catalytic properties of the hydrogel matrix. Incorporating

bacteria into the GO hydrogel further enhances its performance by leveraging the metabolic activity of microorganisms for biodegradation. This synergistic combination allows for efficient adsorption and biodegradation within a single system, leading to enhanced dye degradation and overall textile wastewater treatment efficiency.

After conducting a comprehensive literature review several key findings and trends have intruded. This review highlights several research gaps that need further inquisition, which are given below.

1. Inadequate investigation on strategies to improve the biodegradation rate of recalcitrant dyes in comparison to conventional treatment methods, highlighting the need for innovative approaches to enhance the efficiency of dye degradation processes.
2. There is a significant research gap in investigating strategies to enhance and sustain bacterial activity under high organic loading rates.
3. Limited studies have utilized ^{1}H NMR spectroscopy to investigate the biodegradation pathways and transformation products of dyes,
4. The incorporation of hybrid techniques, such as combining photocatalysis and biodegradation, for the mineralization of textile dyeing effluents represents a highly desirable and underexplored research field.
5. The underexplored use of bacterial cell entrapment as a novel approach for dye degradation.

2.6 Research Objective

The overall objective of this study is to investigate and develop advanced technology that combines with bioremediation for efficient and sustainable treatment of recalcitrant complex dyes from textile wastewater. The integration of advanced techniques contributes towards the development of efficient and environmentally friendly remediation of complex dyes along with

the mitigation of major challenges associated with them. The research objectives of the present study are as follows:

1. Efficient Biodegradation and Detoxification of recalcitrant dyes from textile wastewater using potential microbial consortia.
2. Develop strategies to enhance the biodegradability index of textile wastewater containing recalcitrant complex dyes by implementing AOPs based pre-treatment techniques.
3. Design and performance assessment of a hybrid system (i.e., Photocatalysis and Bioremediation) for efficient dye degradation.
4. Assess the effectiveness and performance of the advanced materials (Graphene Oxide-Calcium Alginate-based hydrogels) for the entrapment of microbes towards complex dyes mineralization.