Chapter 1

An Overview on coloured pollutants, dyes and TiO_2 based photocatalysts

Abstract:

This chapter gives a basic understanding of the coloured pollutants, dyes and TiO_2 based photocatalysts Further, based on its understanding, the undergoing areas of research, observed gaps in research work, outline or objectives of research work backed by detailed literature evidences are proposed. Further, the structure of the thesis followed to achieve the research objectives is outlined.

1.1 Background:

Environmental pollutants pose a significant global challenge, emphasizing the crucial need for natural water conservation to safeguard the land and ensure a sustainable future for upcoming generations. The environmental impact of various industries, including textiles, paper, cosmetics, food, and leather, which release wastewater into the ecosystem has been highlighted by Mulushewa [1]. Among these, the textile industry is a major contributor, the largest water consumer, and a significant wastewater source. The wastewater produced by textile factories is a pivotal contributor to water pollution [2], containing chemicals, suspended solids, toxic compounds, and dye stuff, demanding heightened attention.

The textile industry, recognized as one of the most labour-intensive sectors, is poised for significant growth due to global population increase and escalating consumer behaviour. This growth, however, comes with environmental challenges. Historically, the textile and clothing industries have played a pivotal role in the industrialization of countries,

particularly in developing regions of Southeast Asia and Africa. The migration of these industries to such areas has been driven by increasingly rigorous effluent standards in countries of their origin, where conventional technology struggles to meet standards of economic benefits. Furthermore, the textile sector, being labour-intensive, finds cost advantages in developing nations with comparatively low labour expenses [3,4].

However, the textile industry is paradoxically recognized as the second-largest water-polluting industry [5]. The production of 1 kg of fabric requires approximately 150 L of water, resulting in substantial wastewater discharge into water bodies, particularly in processes like dyeing or printing [6]. A significant concern with textile wastewater is its undesirable colour, which directly correlates with how humans perceive water quality. Even when pollutant content is relatively small, an unappealing colour can create the perception of pollution. Textile wastewater often exhibits this undesired colour, posing a challenge to water quality perception [7].

The relationship between colour and pollutants, quantified as chemical oxygen demand (COD), is complex. While degradation of colour contributes to the reduction in COD content, as colouring agents contain numerous organic substances, it is essential to note that decreasing COD does not necessarily equate to colour degradation. This is especially true when employing a biological process that may not entirely remove dyes [8]. Hence, addressing the textile industry's environmental impact involves reducing pollutant levels and effectively managing and treating the vivid colours associated with textile wastewater.

The improper disposal of wastewater by the textile industry has led to severe water pollution, emerging as one of the most critical global challenges. Despite the significant economic contributions of the textile sector, it also inflicts substantial environmental harm [9]. In particular, wastewater laden with dyes has emerged as an important

environmental pollutant, posing threats to ecosystems and human health. Textile operations generate large quantities of brightly coloured wastewater containing persistent contaminants [10]. Globally, synthetic dyes are produced at a staggering rate of approximately 7×10^5 tonnes annually, with textile industries accounting for over 100,000 tonnes of this total [11].

Approximately 10–15% of the dye is lost during the dyeing process, finding its way into wastewater [12]. The production of textile industries, particularly in developing countries, has led to a surge in the direct or indirect discharge of wastewater containing dyes into the environment. This contaminated water poses a severe threat to both human health and the well-being of animals due to its high toxicity. Addressing and mitigating the impact of these industrial wastewaters on the environment is imperative for the overall well-being of ecosystems and the health of living organisms [13].

In India alone, the dyestuff industry contributes around 60,000 metric tons, representing approximately 6.6% of the global colorant consumption. The primary consumer of these dyes is the textile industry, accounting for two-thirds of the total dye production. Unfortunately, these industries discharge substantial volumes of dye-laden water into water bodies. The extensive use of dyes across various sectors poses a significant danger to the environment and human health due to their non-biodegradable and elevated toxicity levels.

In India, workers in the dye industry face an elevated risk of developing tumors. The mortality rate among factory workers, specifically from cancers, cerebrovascular disease, and lung disease, is significantly 40 times higher for the same ailments compared to the general population [14]. Consequently, it becomes imperative to address the removal or reduction of dye content from industrial effluents before discharge. Thus, before delving into the discussion on removing dyes from water bodies, it is essential to provide a brief

overview of the types and characteristics of dyes.

1.2 Dyes and wastewater

A dye is a coloured substance that naturally attracts and adheres to the substrate to which it is applied. According to Thambiliyagodage [15], dyes impart colour to textiles, carpets, leather, paper, plastic, or wax during the application process. A dye molecule typically comprises two essential components: chromophores and auxochromes. Chromophores are responsible for generating the colour, while auxochromes act as supplementary elements, rendering the molecule soluble in water and enhancing its affinity to attach to fibers, facilitating practical application and coloration.

In the textile industry, various types of dyes are employed, and they are typically classified based on both their application and the dyeing mechanism. These classifications are widely adopted in the textile sector to categorize dyes based on their specific uses and the mechanisms involved in the dyeing process. The categorization is instrumental in facilitating a comprehensive understanding of the diverse dyes in textile applications, allowing for effective selection and application in different contexts.

1.3 Classification of dyes

Dyes can be classified in several ways, such as source of materials, chemical compositions, structure, solubility, and application. However, the structural classification of dye is most appropriate since the group and characteristics of dye can be readily identified. Moreover, based on chemical structure colour index number (C.I. number) is assigned to a dye. A dye with C.I. number has some basic details such as name, purity, chemical composition, price, etc. So, the classification of dyes is given below [16].

1.3.1 Acidic dyes

Water-soluble acidic dyes, characterized by their excellent light fastness, exhibit high water solubility due to the presence of sulphonic acid groups, typically in the form of

sodium sulphonate salts. This chemical composition enhances the dye's solubility in water. Acidic dyes encompass various chemical classes, including azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso. These versatile dyes find application in colouring a range of materials such as nylon, wool, silk, modified acrylics, paper, and leather, as well as in the food and cosmetics industries.

1.3.2 Vat dyes

Vat dyes are renowned for their superior colour fastness, displaying outstanding light and wet fastness properties [17,18]. Predominantly solvable in warm water, some variants exhibit solubility in the presence of minimal Na_2CO_3. The main chemical class of these dyes comprises anthraquinone, including indigoids and polycyclic quinones. Vat dyes are characterized by multi-ring systems that enhance the Van der Waals forces between the dye and the fiber. They find application in colouring cotton, cellulosic fibers, rayon, and wool. Primarily designed for cellulosic fibers due to their strong affinity for these fibers, their application on nanofibers remains unexplored. Indigo, categorized as a vat dye, is denoted by its Colour Index number C.I. Vat Blue 1. Indigo, or indigotin, the principal natural vat dye, is present as its glucoside, indican, in various indigo plant species, such as Indigofera [19].

1.3.3 Reactive Dyes

Reactive dyes feature chromophoric groups such as azo, triarylmethane, anthraquinone, formazan, phthalocyanine, oxazine, etc. These dyes establish a covalent bond with the fiber, rendering them highly permanent. The covalent bonds formed between reactive dyes and natural fibers contribute to their exceptional durability. Notable reactive dyes, including Procion MX, Drimarene K, and Cibacron F, are particularly user-friendly as they can be applied at room temperature. Reactive dyes, known for their effectiveness,

are the preferred alternatives for the purpose of dyeing cotton and other fibers, whether at home or in an art studio.

1.3.4 Disperse dyes

Disperse dyes exhibit limited solubility in water, yet they can form dispersed particles by interacting with polyester chains. The general structure of disperse dyes is planar and non-ionic, featuring attached polar functional groups like -NO_2 and -CN. This planar shape facilitates the dye's movement between densely packed polymer chains, while the polar groups enhance water solubility, improve dipolar bonding between the dye and polymer, and influence the coloration of the dye. Disperse dyes typically contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups. Their primary application is in coloring polyesters, although they also find limited use in dyeing cellulose acetates, acrylic fiber, and polyamides.

1.3.5 Solvent dyes

Except for water, these dyes are solvent-soluble and generally non-polar or little polar, i.e., they do not have sulfonic acid or carboxylic acid group in their structure. Sudan III, Sudan IV, Sudan black B, and oil red O are commonly known solvent dyes. The principal chemical classes are predominantly azo and anthraquinone. Solvents dyes are used for plastics, gasoline, lubricants, oils, and waxes.

1.3.6 Direct dyes

The term "direct dye" signifies that these dyes do not necessitate any fixing agent. These dyes comprise polyazo compounds supplemented by stilbenes, phthalocyanines, and oxazines. The inclusion of sulphonate functionality enhances their solubility in water. The predominant drawback associated with direct dyes is their limited fastness during washing. Despite this limitation, their cost-effectiveness makes them popular for items

that may not require significant washing fastness. The wash fastness can be enhanced by employing direct dyes containing -NH_2 functional groups and sulphonate groups. These dyes are extensively used in the coloring of cotton and rayon, as well as in the dyeing processes of paper, leather, and nylon. They exhibit a high affinity for cellulosic fibers. Industries such as textile, carpet, paint, paper, leather, food, and medicine commonly utilize the aforementioned dyes, generating substantial volumes of wastewater laden with dyes. Consequently, there is a pressing need for an efficient and cost-effective technique to remove or reduce these dyes from wastewater, ensuring that the discharged water complies with permissible environmental norms.

1.3.7 Cationic dyes:

Cationic dyes are classified as water-soluble dyes, producing colored cations in solution, earning them the designation of cationic dyes. These dyes feature cationic functional groups in their structure, such as $=NR_2^+$ or $-NR_3^+$. The primary chemical classes include diazahemicyanine, cyanine, triarylmethane, thiazine, hemicyanine, acridine, and oxazine. They find application in coloring paper, modified nylons, modified polyesters, polyacrylonitrile, and medicinal products [19]. These dyes are typically employed on acrylic, paper, and nylon substrates, with potential applications on specific modified polyester. These dyes feature a quaternary amine group, which commonly constitutes an essential component of formula, although its presence is not always organised. Occasionally a Sulphur atom or positively charged oxygen may substitute for nitrogen in the structure [20].

1.4 Methylene blue Dye:

The methylene blue dye, with the other name Methyl-Thioniniumchloride and IUPAC name 7-(Dimethylamino)-phenothiazin-3-ylidene-dimethyl-azonium chloride exhibits a heterocyclic aromatic structure that is planar. It possesses a molecular weight of 319.85

g/mol and the chemical formula $C_{16}H_{18}N_3S$ and the structure is shown in Figure 1.1 and Identified as a common blue, cationic, and thiazine dye [21], detailed physicochemical parameters of the MB dye are provided in Figure 1.1. Industrially, methylene blue is extensively used in the garment and textile sectors for coloring various textiles [22]. Additionally, it is employed in the dyeing of paper and leather.

Furthermore, dye plays a role in aquaculture, where it treats various fish illnesses [23,24]. While methylene blue (MB) has demonstrated certain medical benefits when administered safely and under professional guidance [10], caution is warranted, especially in contrast to ingestion via polluted water. Discharging partially or untreated wastewater containing MB dye from the mentioned industrial sectors may give rise to substantial health risks. In humans, exposure to MB dye can lead to cyanosis, tissue necrosis, Heinz body formation, vomiting, jaundice, shock, and an elevated heart rate [25]. Furthermore, the presence of MB raises severe concerns for plant life, resulting in growth suppression and reduced pigment and protein content in microalgae such as Chlorella vulgaris and Spirulina platensis [26]. It underscores the importance of properly handling and disposing of MB-laden wastewater to mitigate potential adverse effects on human and environmental health. The adverse effects linked to wastewater loaded with methylene blue (MB) underscore the necessity for effective removal before industrial discharge. Additionally, the discharge of untreated MB dye into water bodies has recently been linked to the scarcity of fresh water in humanity [21]. This issue is particularly prevalent in developing nations where a significant wastewater is dumped into the environment lacking proper management practices [27]. Given the environmental challenges posed by MB dye, scientists have been actively seeking methods to remediate its impact and eliminate MB dye from the environment.

Despite the undeniable relevance of MB in various industries, its potential harm to human

health at specific concentrations due to substantial toxicity [28] and its recalcitrant nature pose a substantial threat to ecosystems and human well-being [29,30]. Thus, addressing the responsible discharge of MB-laden wastewater becomes crucial in safeguarding both environmental and human health.

Table 1.1 Some physio-chemical properties of MB.

S.N.	Parameters	Values/names
1.	Wavelength of maximum absorption	663 nm
2.	Another name	Swiss Blue
3.	Ionisation	Basic
4.	Degree of solubility	3.55%
5.	Color index name	Basic Blue 9
6.	Color index number	52015
7.	Aqueous pH	2-3.5

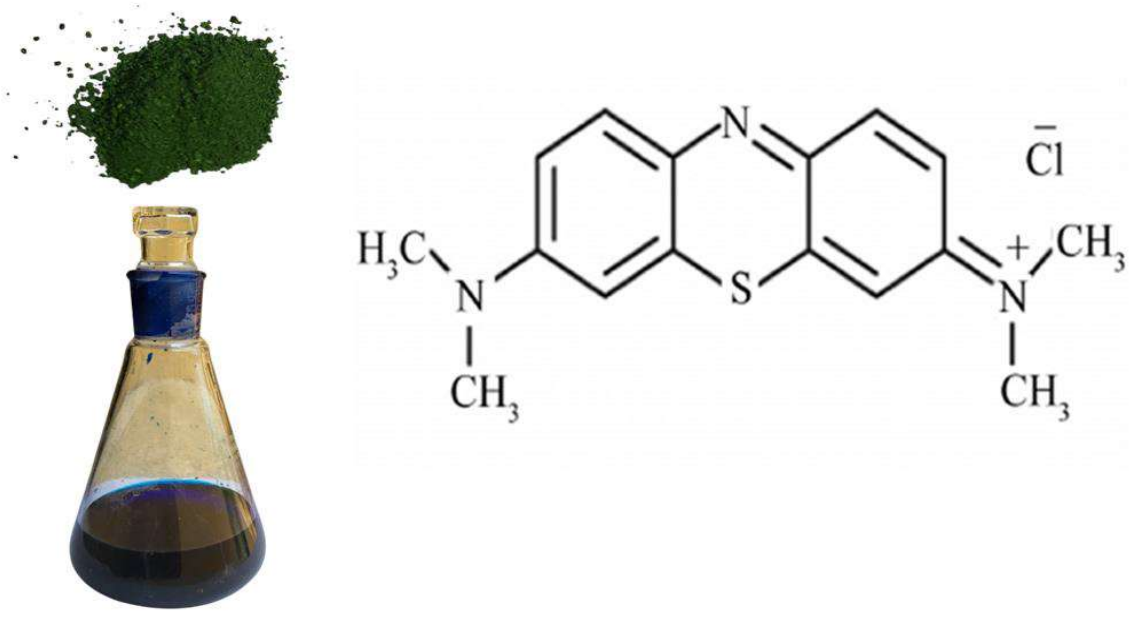

Figure 1.1 Physical Appearance and molecular structure of Methylene Blue

1.5 Conventional methods to treat dye-contaminated water

The conventional methods, including physical, chemical, and biological, such as absorption, adsorption, coagulation and flocculation, precipitation, filtration, and ion exchange, were investigated to remove/reduce dyes from the wastewater. While conventional treatment methods are still employed to effectively remove a significant portion of contaminants from wastewater [31]. The growing concern about water scarcity has prompted the demand for water reuse. This has led to an emphasis on more through purification of wastewater. While effective, primary and secondary treatments have proven insufficient to enhance water quality to a level suitable for residential and industrial use [32]. Consequently, advanced treatment methods have been developed. They can be applied post-secondary treatment to facilitate the additional removal of organic pollutants, hazardous chemicals, or other nutrients in lower quantities, addressing the need for more comprehensive water purification [33]. These methods include ozonation, photocatalysis, and Fenton. Photocatalysis is one of the important advanced oxidation processes. A brief description regarding this is given below.

Advanced oxidation processes (AOPs) represent an eco-friendly approach for eliminating a wide array of pollutants, encompassing air and water pollutants such as aromatics, petroleum-based contents, petroleum hydrocarbons, chlorinated hydrocarbons, pesticides, insecticides, volatile organic compounds (VOC), dyes, and various organic materials [34]. AOPs rely on creating reactive oxygen species, notably, hydroxyl radicals characterized by an unpaired electron, resulting in their short life spans. This characteristic enables them to actively and rapidly engage with diverse chemical species that are typically challenging to degrade. AOPs standout compared to conventional methods due to their capacity to generate thermodynamically stable oxidation products, including carbon dioxide, water, and biodegradable organics. Among the AOPs,

photocatalysis is a significant process that harnesses a source of radiation including sunlight using a photocatalyst. These photocatalysts have proven effective in addressing environmental pollution and energy crises across different segments of the solar spectrum [35,36].

1.5.1 Photocatalysis

The AOPs has been extensively researched over the past five decades to eradicate harmful microorganisms, pigments, contaminants, and toxic substances from polluted water [37]. Photocatalysis, a term derived from "photo" (light) and "catalysis," involves using light to enhance the rate of chemical reactions. by reducing the activation energy required for the primary reaction to commence [38]. In catalysis, a substance, referred to as a catalyst, is introduced into the reaction, accelerating reactants' transformation into products without any change. The photocatalysts are semiconductors in nature [39]. A critical distinction between conventional catalysis and photocatalysis lies in using photons or light instead of heat to activate the catalyst. Therefore, photocatalysis involves the activation of the catalyst through light application, leading to an improved reaction rate without self-involvement. The photocatalysts used for degradation of organic matter including dyes are discussed below:

1.6 Photocatalyst

A photocatalyst is a substance that absorbs light, causing its electrons to become excited and raise their energy levels. This process creates e^-/h^+ pairs, which facilitate chemical reactions without the photocatalyst itself being consumed. The excited electrons transfer their energy to another substance, driving the reaction forward [40,41]. Notably, in 1938, titanium dioxide (TiO_2) was first employed as a photosensitizer to bleach dyes in the presence of molecular oxygen. Subsequently, in 1972, Fujishima and Honda documented photo-induced water oxidation using TiO_2 electrodes under ultraviolet (UV) light. Around

the same time, Frank and Bard reported the photodecomposition of pollutants such as CN^- and SO_3^{2-} mediated by TiO_2, ZnO, and CdS [42].

Many photocatalysts such as CdSe [43], SiC [44], GaP [45], TiO_2 [46], GaAs [47], CdS [48], ZnO [49] and g-C3N4 [50] etc. are reported and used in AOPs for degradation of dye. Among these photocatalysts, TiO_2 is one of the most suitable photocatalysts due to its unique photoresponse towards UV/vis light.

1.6.1 TiO_2 photocatalysts

TiO_2 stands out as one of the most extensively studied semiconductors in photocatalytic applications due to its wide distribution, easy synthesis, low cost, stable chemical properties, non-toxicity, and high efficiency, which is why it is considered a benchmark in the field of photocatalysis [51]. Other advantages include high photo-reactivity, biological inertness, and environmentally friendly merits. Its remarkable efficacy in catalyzing processes such as H_2 evolution, pollutant removal, and CO_2 reduction is attributed to its exceptional chemical stability, ample surface area, biocompatibility, abundance, and resistance to photo corrosion. Furthermore, the uncomplicated synthesis method and the ability of the redox potentials of photo-induced electrons (e^-) in the Conduction Band and holes (h^+) in the Valence Band to be appropriately negative and positive, respectively, enable photoexcited electrons and holes to serve as acceptors and donors [52,53].

Titanium dioxide (TiO_2) exhibits three distinct phases: anatase, rutile, and brookite [54]. Anatase and rutile phases possess a tetragonal crystal structure, while brookite has an orthorhombic crystalline structure (Figure 1.2). Thermodynamically, rutile stands as the most stable phase of TiO_2, whereas anatase and brookite are considered metastable. At elevated temperatures, the anatase and brookite phases of TiO_2 can undergo conversion into the rutile phase [55]. All the three phases of TiO_2 (anatase, rutile and brookite) have

three crystal faces. The faces (101), (001) and (100) are the faces of anatase. The first two of them, i.e. (101) and (001) are low energy surface. These faces very are common for natural crystals. The face (101) is most popular face of anatase nanocrystal while the surface (100) is very rare [56].

The crystal faces (110), (100) and (001) belong to rutile structure. In this phase also first two, i.e. (110) and (100) are low in energy surface. Thermally, the face (110) is most stable while (001) is less stable and restructuring occurs above 450°C [57].

The three crystal faces of brookite are (010), (110) and (100). Among these faces, the face (010) has low stability, whereas (100) is highly stable [58].

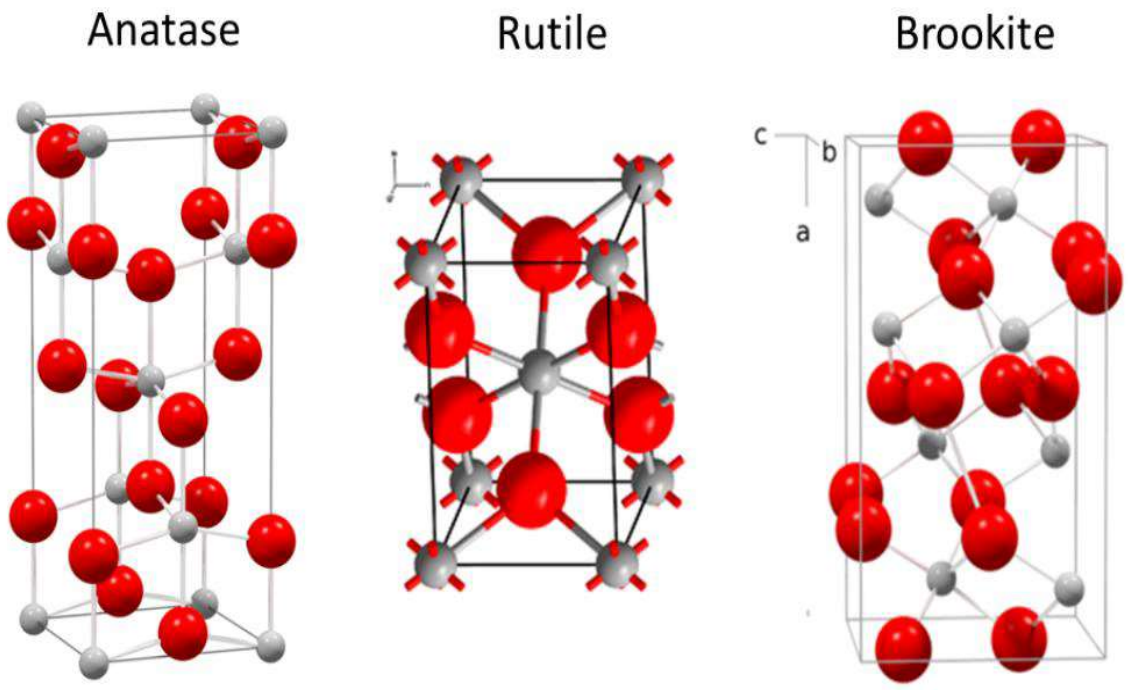

Figure 1.2 Crystal structures of TiO_2 Anatase (tetragonal), Rutile (tetragonal) and Brookite (orthorhombic) polymorphs [94]

Despite these advantages, TiO_2 is characterized by a wide bandgap, confining its light absorption to the UV region, constituting only 4% of the solar spectrum. This limitation

results in suboptimal photocatalytic efficiency [59]. Additionally, the rapid recombination of photo-induced electron-hole pairs presents another drawback, significantly diminishing the overall photocatalytic effectiveness of pure TiO_2.

1.6.2 Synthesis technique of TiO_2 nanoparticles

1.6.2.1 Hydrothermal method

The hydrothermal technique involves the production of nanoparticles in the presence of water, utilizing elevated temperature and pressure. This method is particularly effective for substances that are typically insoluble in water under normal conditions (<100°C and 1 atm). When synthesizing TiO_2 nanoparticles through this approach, several factors come into play, including temperature, pressure, duration of the experiment, type of solvent, pH level, and the initial charge of the product.

1.6.2.2 Micro emulsion technique

In this method, two phases composed of two liquids that don't mix well are blended and stabilized using a surfactant, sometimes with an additional cosurfactant. Micro-emulsions are not stable in terms of thermodynamics and typically have droplets ranging from 5 to 100 nm in size. Depending on the surfactant's characteristics, micro-emulsions can be formed as either water-in-oil (W/O) or oil-in-water (O/W). In water-in-oil (W/O) micro-emulsions, water droplets are surrounded by a continuous oil phase, whereas in oil-in-water (O/W) micro-emulsions, oil droplets are surrounded by an aqueous phase. Both types of micro-emulsions are stabilized by surfactants and cosurfactants, which work to minimize the interfacial tension between the two phases to nearly zero. The stability of micro-emulsions is influenced by factors such as particle size, particle-particle interaction, and particle-water interaction.

1.6.2.3 Biological method

In this approach, nanoparticles are produced with the assistance of microorganisms such as bacteria (e.g., *Pseudomonas deceptionensis, Weissella oryzae, Bhargavaea indica*), fungi (e.g., *Neurospora crassa, Actinomycetes*), and yeasts (e.g., *Yarrowia lipolytica NCYC 789, Extremophilic yeast*), among others. Microorganisms possess the capability to reduce metal salts to metal nanoparticles with a narrow size distribution and reduced polydispersity owing to various reductase enzymes [60].

1.6.2.4 Spray pyrolysis

This process involves the synthesis of a nanostructure by spraying or injecting a precursor solution onto a hot substrate within a furnace, utilizing a nano-porous nebulizer. The precursor undergoes decomposition, resulting in the formation of the desired final material on the substrate. Control over nanostructural parameters such as particle size, shape, and thickness is achieved by adjusting factors like spray energy, duration of spray, distance between the spray gun and the substrate, as well as the temperature of the furnace and substrate, which can be managed using manual or automated control systems [61].

1.6.2.5 Co-precipitation method

Co-precipitation reactions involve several simultaneous processes including nucleation, growth, coarsening, and/or agglomeration. These reactions lead to the formation of a precipitate from a homogeneous liquid phase due to physical changes such as temperature, pH, and reactant concentration. In a typical co-precipitation reaction, two or more water-soluble salts react with each other, resulting in the formation of one or more water-insoluble salts in the liquid phase. Precipitation occurs when the concentration of these products exceeds the solubility product value in the reaction medium. Slow precipitation typically results in the formation of small particles, whereas fast precipitation leads to the formation of larger particles of the photocatalysts [62].

1.6.2.6 Sol-gel method:

The photocatalysts prepared by sol-gel route exhibit high crystallinity, purity, and superior quality, along with better homogeneity compared to traditional powder synthesis techniques, all achieved at lower processing temperatures. In this process, sols, which are dispersions of colloidal particles in a liquid, are transformed into gels, forming an interconnected, rigid network with pores of sub-micrometer dimensions and polymeric chains whose average length exceeds a micrometer. Sol-gel processing offers precise control over the structure of a material at the nanometer scale, owing to the mixing that occurs on an atomic scale.

In sol-gel method, four steps are involved.

1. Hydrolysis of precursors.
2. Condensation (gel formation).
3. Drying.
4. Calcination.

In the hydrolysis step of the sol-gel method, precursors are typically dissolved in water or alcohol. The hydrolysis process is facilitated by the addition of acid or base. During the condensation step, continuous mixing of the precursor and solvent leads to the formation of a gel. Subsequently, in the drying step, the solvent is removed from the gel at a specific temperature, while organic precursors decompose at higher temperatures during the calcination step.

One of the key advantages of the sol-gel technique is its ability to tune the size of nanoparticles by controlling factors such as solution composition, pH, and temperature. Additionally, the sol-gel method offers advantages including high product homogeneity, precise control over the size and shape of the resulting nanoparticles.

1.6.2.7 Solution-Combustion Method:

Solution Combustion Synthesis (SCS) is a self-sustained thermal process that derives its heat primarily from combustion reactions, distinguishing it as a specialized form of Self-Propagating High-Temperature Synthesis (SHS) or Combustion Synthesis (CS). In SCS, the components are mixed at the molecular level in an aqueous solution, unlike SHS, where powders are mixed on the micro-level. Typical fuels used in SCS, can include compounds like urea, glycine, and citric acid. These fuels not only provide the necessary heat for the reaction but also form stable complexes with metal ions, enhancing their solubility and preventing selective precipitation during water removal. The process involves self-sustained redox exothermic reactions between hydrated metal nitrates and fuels, driven by the system's need to reduce its Gibbs free energy, thus converting chemical potential into heat. SCS has three key features distinguishing it from other CS types: The SCS process involves molecular-level mixing and primarily generates heat from organic fuel combustion. It produces large gaseous byproducts, causing significant solid expansion and rapid cooling, resulting in porous materials. The process starts with solution dehydration and thermal decomposition, followed by exothermic reactions, yielding at least one solid product and a large volume of gas. This method enables the synthesis of a variety of nanoscale materials, including oxides, metals, alloys, and sulfides, which are crucial for many modern applications [63].

1.6.3 Modification of TiO_2 photocatalyst

Over the past two decades, numerous efforts have been focused on enhancing the photocatalytic effectiveness of modified TiO_2 when exposed to UV light. Various strategies have been employed to achieve this objective which includes doping, co-doping, carbon composite, organic coating and quantum dots [51][64]. One approach involved doping to prevent the recombination of photogenerated charges. However, the

efficacy of doped TiO_2 is significantly influenced by the type and quantity of doping species [65].

According to recent studies, adding a dopant material into TiO_2 nanoparticles enhanced their photocatalytic performance. Doping may result in a surface defect with an increase in electron-hole pairs that may result in the generation of hydroxyl groups at the photo catalyst's surface. The remarkable activity of the hydroxyl radicals in oxidation reactions would enhance photocatalytic efficiency [14] . But apart from doping, co-doping through two distinct types of elements has become highly beneficial for the enhancement of the photocatalytic activity of TiO_2. In this method, incorporating various dopants increases the absorption of visible light and makes it more difficult for photogenerated charge carriers to recombine [15]. There are many metals, such as Fe [66] , Cu [67], Ag [68], and Sn [69] which are used as a dopant. Among them, transition metal ions are extensively used to increase the photocatalytic performance of TiO_2 nanoparticles because of their advanced capability to reduce the rate at which recombination of pairs of e^-/h^+ occurs [19], and rare earth metals have been significant consideration because of their distinct electronic arrangement of the f sub-shell [21–23].

Apart from metals, non-metals are also doped in TiO_2 because of their ability to diminish Eg, enrich visible light absorption, and upsurge the separation rate of pairs of e^-/h^+ during photocatalytic response [24]. TiO_2 doped with non-metal atoms showed more excellent absorption from visible light. Supplementary electronic states above the valence band of bare TiO_2 have been discovered in TiO_2 doped with non-metals. These electronic states are accountable for the red-shift absorbance and the reduced oxidation potential of non-metal-doped TiO_2 [25]. Non-metals such as nitrogen [26,27], sulfur [28], iodine [70–73], carbon [42], and fluorine [74] have been widely studied.

A brief literature survey regarding metal, non-metal, and co-dopant of TiO_2 photocatalysts

by the solution-combustion method are given in Table 1.2.

Table 1.2 Literature survey regarding dopant selection

S.N.	Dopant	Dopant Level	Pollutant	Initial conc.	Results	Ref.
1.	Fe	0.3%wt	Methyl Orange	30 ppm	96% degradation in 2h under UV light	[75]
2.	Fe-Pr	0.17% Fe and 0.69% Pr mole	Acid Orange 7	10 ppm	87% degradation in 1h under visible light	[76]
3.	Fe	2% mole	Acid Orange 7	34 ppm	88.7% degradation in 3h under UV light	[77]
4.	Eu	0.1% wt	Amido Black	10 ppm	99% degradation in 25 min under UV light	[78]
5.	Bi	1% wt	MB	50 ppm	80% degradation in 2h under a mercury vapor lamp	[79]
6.	Fe-N	1% Fe & % N	MB	10 ppm	80.5% degradation in 5h under visible light	[80]
7.	Na	8% mole	MB	5 ppm	92.5% MB degradation in 1h under UV light	[81]
8.	La-B	1% mole	AO7	20 ppm	93% degradation in 5h under visible light	[82]
9.	C	1% mole	MB	10 ppm	56.25%, 51.18% and 62.95% degradation in 8h under UV, visible and solar lights, respectively	[83]
10.	I	7% mol	Rhodamine B	20 ppm	93% degradation in 3h under sunlight	[70]
11.	Fe-Ce	0.5%	MO	50 ppm	20% degradation in 4h under visible light	[84]
12.	Fe-Er	1.25Fe/ 1.5Er	Bisphenol A	10 ppm	75% degradation in 4h under visible light	[85]
13.	Fe	5% mol	Direct Blue 199	300 ppm	Under UV and visible light	[66]
14.	I	3% mol	Direct Blue 199	300 ppm	Under UV and visible light	[86]
15.	Fe	10% mol	MB	20 ppm	75% degradation in 3h under visible light	[87]
16.	Ni-La	5% Ni and 3% La wt.	Reactive Yellow-145	20 ppm	96.5% degradation in 1h under visible light	[88]
17.	Cu-S	0.4% Cu– 0.5% S	ciprofloxacin	10 ppm	97.6% and 100% degradation in 2h under UV light and visible light, respectively	[89]

1.7 Regeneration of used photocatalysts

Regenerated TiO_2 nanoparticles are crucial for sustainable photocatalysis, enhancing their reusability and cost-effectiveness. In Table 1.3 there are some researches related to regenerated photocatalysts are given:

Table 1.3 Previous Literature Regarding Regeneration of Photocatalysts

Catalyst	Regeneration Method	Reference
TiO_2	Sol-gel	[90]
P-25 photocatalysts	Water washing, H_2SO_4 washing, NaOH washing, and thermal treatment	[91]
4% Fe-doped TiO_2	Solution-Combustion	[92]
5% Fe-doped TiO_2	Solution-Combustion	[66]
3% I-doped TiO_2	Solution-Combustion	[86]

1.8 Conclusion From literature search

- TiO_2 photocatalysts can be synthesized by sol-gel method.
- La and I are selected as a dopant and La-I co-dopant.
- Dye can be photodegraded by TiO_2 based photocatalysts.
- The activity of TiO_2 can be enhanced by doping of metals and non-metals.
- TiO_2 can be regenerated after dye degradation.

1.9 Research Gap:

- Citric acid assisted synthesis of La-I co-doped TiO_2 photocatalysts is not reported yet.
- Citric acid assisted synthesis of La doped TiO_2 photocatalysts is very rare.
- Study on regeneration of La doped TiO_2 & La-I co-doped TiO_2 photocatalysts are not reported yet.

- Phytotoxicity study of La-I co-doped TiO_2 photocatalysts are not reported yet.

To fulfil the research gaps the objectives of the present study were set as:

1.10 Objectives and Approach

The objective of the present study is to evaluate the effect of anions and cations doping and co-doping on the photocatalytic efficiency of TiO_2 for the degradation of MB dye from its aqueous solution.

1. Synthesis and Characterization of La, I doped, and La-I co-doped TiO_2 photocatalysts.
2. Photocatalytic dye degradation from its simulated dye solution using the synthesized photocatalysts in UV photochemical reactor.
3. Determination of dye degradation rate in the photocatalytic process by kinetic studies in UV PCR reactor.
4. Regeneration of used photocatalysts and determination of their photocatalytic activity regarding the dye degradation.
5. Comparison among photocatalysts (undoped TiO_2, La/I doped TiO_2, La-I co-doped TiO_2, and Aeroxide P-25) for dye degradation.

The different photocatalysts i.e. pristine, La-doped, I-doped and La-I co-doped TiO_2 nanoparticles were synthesized from TiO_2 powder using citric acid assisted sol-gel method with modification of reported method by Madhvi [93], Sudhakar [66] These nanoparticles were characterized by standard procedure. The kinetics of photodegradation of MB dye was studied in a photocatalytic batch reactor. The used best photocatalysts were regenerated and its reusability was tested. The comparison of performance of different photocatalysts was also done.

1.11 Structure of the thesis:

The thesis is structured in the following manner-

Chapter 1 provides the extensive background in the form of a detailed literature overview, thereby setting strong validation for the proposed research objectives.

Chapter 2 provides general insights into the experimental procedure to be followed to conduct the photocatalytic degradation of MB dye using prepared and regenerated photocatalysts in the photochemical reactor. This basic understanding will be further helpful in getting a clear picture from the brief specific experimental details corresponding to each set of experiments that will be given in the subsequent chapters.

Chapter 3 covers the synthesis of TiO_2 doped with La using inexpensive TiO_2 powder by straightforward citric acid-assisted solution-combustion procedure and annealing to increase the crystallinity of the nanoparticles. The conditions under which the nanoparticles were prepared significantly impacted their size and form. The activity of nanoparticles as photocatalysts was determined by the kinetics photodegradation of MB dye. The reusability of photocatalysts was also performed in 5 cycles. This dye was chosen because it is frequently found in textile effluent and exhibits excellent chemical and biological resistance to degradation by traditional processes.

Chapter 4 focuses on synthesising pristine and Iodine-doped TiO_2 (IDT) nanoparticles utilising cost-effective TiO_2 powder. The synthesis process involves a solution combustion method using citric acid as a fuel and subsequent calcination to enhance the crystallinity. It should be noted that the preparation conditions employed in this study significantly impacted the particles' size and morphology.

The MB dye degradation in the UV Photochemical reactor formed the basis for assessing the photocatalytic capabilities of the catalysts. Additionally, the regeneration of the catalysts was repeated five times to evaluate their photocatalytic activity. Factors such as

pH, catalyst dosage, and initial dye concentration were investigated to optimize their impact. A germination test was conducted using *Vigna radiata* seeds to assess the appropriateness of the photocatalyst-treated MB solution for irrigation. The test involved treated dye water, distilled water, and untreated dye samples, providing insights into the potential reusability of the wastewater.

Chapter 5 describes the solution-combustion synthesis of La and I co-doped TiO_2 (LICT) photocatalysts with various molar ratios. This method creates fine TiO_2 particles by limiting their growth, which is easy and cheap. Citric acid was utilized as fuel to aid in the preparation of nanoparticles. Several techniques were used to characterize phase compositions, optical properties, and crystalline structure of the LICT. The degradation of the MB dye in the UV Photochemical reactor served as the basis for investigating the photocatalytic performance of the photocatalysts, and the regeneration of photocatalysts was performed 5 times to test their photocatalytic activity. The influence of several variables, including pH, catalyst dose, and initial dye concentration, was studied for optimization. To understand the suitability of the photocatalyst-treated MB solution for irrigation, the germination test on *Vigna radiata* seeds was performed with treated dye water, distilled water, and untreated dye sample, which gives an idea about the wastewater's reusability prospects.

Chapter 6 presents broad inferences and conclusions that elaborate on the significance of the study conducted. Based on the inferences drawn, other recommendations and future directions for the research based on current work are proposed.

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