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Titanium Dioxide (TiO_2) based photocatalysis for textile wastewater treatment – its applications and biosafety – A Review

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Abstract:

Photocatalysis is an efficient method that can be used in wastewater treatment to degrade the toxic dyes released from many textile and other industries. Titanium dioxide has proved to be an efficient photocatalyst that can be used for wastewater treatment. Moreover, it may be very well utilized as an antibacterial agent based on substantial oxidation movement and super hydrophilicity. TiO_2 demonstrates relatively high reactivity and synthetic strength under UV light (λ<387nm), surpassing the bandgap of 3.3eV in the anatase crystalline stage. The improvement of photocatalysts showing high reactivity under visible light (λ> 400 nm) ensures the use of the principal part of the sunlight and therefore be utilized for efficient wastewater treatment. Broad utilization of TiO_2 in various applications has raised many concerns regarding treated dyes and titanium nanoparticles' toxicity. Also, the dye wastewater rich in harmful azo compounds may generate highly toxic intermediates affecting aquatic life forms when treated using photocatalytic methods. Additionally, the nanoparticles may leach into the aquatic environment and may result in toxic effects on both the aquatic environment as well as on humans. This review talks about the potential use of TiO_2 in the photocatalytic treatment of dye wastewater and the toxicities associated with them.

Keywords: Photocatalyst, nanoparticles, Titanium dioxide, Dopants, Wastewater treatment

1. Introduction:

Water pollution is a significant problem worldwide. Most of the water pollution is caused by untreated industrial effluent released into the water bodies. Traditional procedures for wastewater treatment are not adequate any longer to treat highly polluted water. A few techniques, for example, adsorption, biological treatment, oxidation, coagulation, and flocculation, have been examined and found to be very effective [1]. The principal disadvantage of these techniques is the generation of a more potent pollutant containing sludge. However, recent improvements in this field focus on oxidative degradation of the organic compounds that are either dissolved or scattered in fluid media. Among these "Advanced oxidation process" (AOP), heterogeneous photocatalysis is able to mineralize most contaminants completely.

In environmental pollution caused by dyes, the heterogeneous photocatalytic process is an efficient system that can be efficiently applied to oxidize the organic dye pollutants in an aqueous system. An additional cause of dye decolorization can be a self-sensitization mechanism (Figure 1B). Here, the dye particles absorb the light and enable charge exchange by excitation of dye molecule to the conduction band of the semiconductor, which results in the generation of an unstable dye cation radical along with the formation of an active specie on the surface of the semiconductor, which in turn attacks the destabilized dye particle. The manifestation of this mechanism was reported for the first time in 1977, which portrayed effective N-de-ethylation of rhodamine B accumulated on Cadmium sulphide [2]. Similarly, the self-sensitization machinery was further used to explain the mechanism of faster decolorization kinetics for methylene blue in solar light and (undoped) TiO_2 compared to decolorization under UV light [3].

An example of the mechanism involving the self-sensitization of dyes was detailed by Liu *et al.* [4], who demonstrated the photo-oxidation of alizarin red in the presence of TiO_2 and visible light by merging the ESR spin- trapping technique with sub-atomic orbitals estimations. It was discovered that the fundamental dynamic species was O^{2-} or OOH. It was suggested that the atom with maximum electron density at the ground level offers electron for being transferred to the semiconductor surface and presents the place where the attack by the superoxide anion radicals (formed at the semiconductor surface) occurs [4]. Hence, it is possible to contrast the photocatalytic machinery (Figure 1A) and the photo-sensitization machinery (Figure 1B) by the kind of active species and the attack's preferred location in the sensitization mechanism. In another type of photocatalytic system (Figure 1C), accumulation occurs on the dye, as in system B; however, the electrons exchanged to the semiconductor cause the reduction of another particle [5, 6].

A thin bandgap semiconductor combined with a wide bandgap semiconductor, such that the later has a more anodic conduction band, can act as a sensitizer (Figure 1D).

The need to treat the textile wastewater provoked detailed study of photocatalytic degradation of dyes [7–9]. The textile industries account for the discharge of around 15% of the total dye production in the world [10]. The leather tanning industry, the paper and pulp industry, the hair-coloring industry, food industries, etc. are some of the other industries responsible for discharging dyestuffs [11]. Apart from the dye toxicity, the toxicity of the raw materials used to manufacture the dyes (specifically aromatic amines) should also be considered.

Semiconductors are the critical materials in the photocatalytic process, in which Titania plays an excellent example, among others. Research on Titania's use is on the rise, and procedures to purify water and air have been postulated [12]. It is likewise reported as the best and valuable photocatalyst because of its application in the field of wastewater treatment, water, air refinement, change or degradation of pollutants, removal of micro-organisms, etc. This wastewater treatment method using a photocatalytic semiconductor is known as the "Advanced oxidation process" (AOP), which causes total mineralization of the contaminants to carbon dioxide or to more or less toxic compounds, based on the type of intermediates [12].

2. Photocatalysis

2.1 What is Photocatalysis?

Photocatalysis is the fusion of photochemistry and catalysis. The word "photocatalysis" is made out of 'Photo' - light 'Catalysis' is where the catalyst participates in modifying the chemical reaction rate by reducing the activation energy, without any change in catalyst properties [13].

Thus, photocatalysis is a process of utilizing a catalyst used for accelerating chemical reactions in the presence of light. A photocatalyst is characterized as a material that is fit for retaining the light, creating electron-hole pair that empower chemical transformation of the reacting compounds and recover its chemical composition after each cycle of such reactions [14]

2.1.1 Homogeneous Photocatalysis

For the most part, homogeneous photocatalytic forms are utilized with metal complexes (transition metal complexes like iron, copper, chromium, and so on.). This process involves the formation of hydroxyl radicals at a higher oxidation state of metal ions in the presence of light, which later reacts with organic matter resulting in the degradation of toxic compounds.

2.1.2 Heterogeneous photocatalysis

Heterogeneous photocatalysts exist in different phase from that of the reactants. On comparing homogeneous and heterogeneous photocatalytic processes, heterogeneous photocatalysis is an improved strategy that can be utilized to destroy different toxic pollutants [15–17]. The advantages of heterogenous photocatalysis involve (i) complete degradation of toxic compounds, (ii) no waste discharge, (iii) cost-effective, and (iv) mild reaction conditions [15,16,18]. Heterogeneous photocatalysis uses a semiconductor material with a bandgap between an electron's valence state and conduction state, depicted in Figure 2. As shown in the figure, when energy greater than or equivalent to a semiconductor bandgap falls on it, the electrons present in its valence state gain energy and get excited to the conduction band (CB). Lack of an electron in the valence band (VB) results in a positively charged hole. These holes and electrons are unstable and are good oxidants and reductants. This implies they react with oxygen and water to produce strong radicals like $O_2\bullet$- and •OH that causes reduction and oxidation of the contaminant, thus resulting in the formation of water and carbon dioxide via the formation of various intermediates [19]

The arrangement of heterogeneous photocatalysis utilizing semiconductor materials comprises a light-collecting antenna and a few active species to encourage pollutant degradation. The arrangement of chain oxidative– reductive reactions that happen at the photon-activated surface are depicted as:

$\text{Photocatalyst} + h\upsilon \rightarrow h^+ + e-$ (1)

$H^+ + H_2O \rightarrow \bullet OH + H^+$ (2)

$h^+ + OH^- \rightarrow \bullet OH$ (3)

$h^+ + \text{pollutant} \rightarrow (\text{pollutant})^+$ (4)

$e^- + O_2 \rightarrow \bullet O_2-$ (5)

$\bullet O_2- + H^+ \rightarrow \bullet OOH$ (6)

$2\bullet OOH \rightarrow O_2 + H_2O_2$ (7)

$H_2O_2 + \bullet O_2- \rightarrow \bullet OH + OH- + O_2$ (8)

$H_2O_2 + h\upsilon \rightarrow 2\ \bullet OH$ (9)

$\text{Pollutant} + (\bullet OH,\ h^+,\ \bullet OOH \text{ or } O_2-) \rightarrow \text{degradation product}$ (10)

At the point when the semiconductor is illuminated by an input light having ultra-band-gap energy (hυ > Eg), a valence band (VB) electron (e−) is excited to the conduction band (CB), creating a photogenerated hole (h+) at the VB. As a result, the created e−/h+ sets can relocate to the outside of the semiconductor and take part in redox reactions. The photocatalytic reactions generally include three principle active species: a hydroxyl radical (•OH), h+, and a superoxide radical ($\bullet O_2-$), where •OH is the essential oxidant in the photocatalytic degradation of pollutant in the wastewater. The formation of •OH radicals occurs through two routes, (i) H_2O and OH− in the water are readily oxidized by photogenerated h+ to give •OH radicals; (ii) O_2 in the aqueous solution is reduced by photogenerated e− to give $\bullet O_2-$ radicals, followed by reaction with h+ (forming •OOH radicals) and after that undergo further decomposition to create •OH radicals. Besides, the photogenerated h+ is broadly considered as an oxidant for directly disrupting organic pollutants, which relies upon the type of catalyst and oxidation conditions [20]. It is to be noticed that the photo-induced e− can effectively recombine with h+ after their formation without electron or hole scavengers. In such a manner, the presence of specific scavengers is essential for restricting the charge recombination rates and for improving the productivity of photocatalysis.

Semiconductors material used for developing photocatalysts should have a smaller bandgap to enable it to retain solar energy over a broad range of the spectrum. Simultaneously, the semiconductor should have a moderately positive valence band for the generation of h^+ and •OH radicals [21]. Second, the catalyst should have a particular platform/framework for effective charge separation and transportation [22, 23]. Moreover, the semiconductor materials should have excellent photo-electrochemical stability in the electrochemical reactions [24].

2.2 Composite Photocatalyst

The vast majority of the examination on photocatalyst improvement has been done on TiO_2. TiO_2 has a bandgap of 3.2 V; thus, it gets sensitized by radiations in the UV spectrum of the solar insolation. As the UV comprises just approx. 4% of the total spectrum, the focus has now moved to the advancement of photocatalysts that can function in the visible light region which is about 47% of the total spectrum.

The p-n junction rule is well known in semiconductor and photovoltaic standards. The equivalent can be utilized in photocatalysis to isolate the photogenerated electrons and holes and keep them from recombining (Figure 3).

A p-type material has plenty of holes, and an n-type material is rich in electrons. Whenever p-and n-type semiconductors are consolidated, there is a blend of the holes and electrons at the interface. This causes a depletion zone production wherein an electric field is made with a negative charge on the p-side and positive charge on the n-side. This depletion zone and electric field fulfill two needs and help in decreasing recombination. First, the depletion zone is a neutral zone and does not enable more electrons to move and combine with gaps. Furthermore, the electric field set up in the process repels the like charges and does not allow recombination. Many reports elucidate the use of this principle in photocatalysis [26–29].

2.3 Heterojunction coupling

A heterojunction coupling between two photocatalysts is characterized by composite materials with various bandgaps combined to the extent that surface transfer of electrons and holes is made conceivable between them (Figure 2).

When two photocatalytic materials with different bandgap values and band positions are illuminated, the electrons from the particular VBs get excited and come to the individual CBs, creating holes in the VB. If these holes and electrons are not captured and reacted on time, they are lost in recombination. To capture them, these two photocatalytic materials are combined to frame a composite. Then on the formation of composites, the excited electrons present in the material with higher CB get transferred onto the material with a lower position of CB. Additionally, the holes with a lower VB potential get transferred onto the VB of the material with a higher VB potential. In this manner, this interfacial exchange of electrons and holes over a heterogeneous junction isolates them onto distinctive surfaces, which helps in capturing recombination. Instances of such composites are accessible in many reports [30–33].

2.4 **Advantages of Photocatalysis**

The advantages of photocatalysis involve the following [8, 15–17, 34]:

(i) Photocatalysis is more energy-efficient in comparison to other treatment techniques (adsorption, ultrafiltration, reverse osmosis, coagulation, etc.).

(ii) Utilizes a sustainable form of energy, i.e., solar energy, and thus does not cause any pollution.

(iii) Photocatalysis results in the conversion of toxic pollutants to non-toxic compounds, in contrast to conventional treatment methods, and is capable of degrading various hazardous compounds present in wastewater

(iv) Photocatalysis does not require extreme reaction conditions and requires the least chemicals.

(v) Secondary waste generation is minimal.

2.5 Photocatalysis Limitations

The photocatalytic treatment has the following limitations [15–17]:

- Difficulty with interfacial charge transfer, which reduces the photocatalytic activity.
- Requires enhancement of the charge separation in order to reduce charge recombination rate.
- Restriction of charge carrier recombination, decreasing the reaction time.

3 Metal oxides as photocatalyst

There are numerous sorts of photocatalysts. Metal oxide semiconductors are the most appropriate for this purpose as they have moderately wide bandgap energy (Table 1). Another beneficial property is their capacity to oppose photo corrosion [35]. This is essential for the photocatalytic action and lifetime durability.

Metal oxides are formed as an outcome of the coordination ability of metal particles. The oxide ions form a coordination sphere around metal ions and result in the formation of a closed packed structure. The distinctive physical, magnetic, optical, and chemical properties of metal oxides are of great interest to scientists because of the fact that these are very sensitive to change in composition and structure [36].

The transition metals and their compounds are utilized as catalysts in the chemical industry and battery industries. In addition, these compounds can be utilized in the development of interstitial compounds and alloys. The transition metals have the exceptional properties of the development of colored compounds and exhibit magnetic properties. Metals of d-block act as a catalyst, superconducting materials, sensors, ceramics, phosphors, crystalline lasers, etc. Other than these, they are effective photoactive materials and work as photosensitizer [36].

Semiconductor photocatalysts are favored in the photocatalytic treatment of dye wastewater for the various reasons: (i) they are not expensive; (ii) they have low to no toxicity; (iii) show tunable properties that can be altered, for example, by size decrease, doping, or sensitizers; (iv) allow for a multi-electron transfer process; and (v) they are fit for broadening their utilization without significant loss of photocatalytic activity [37- 40].

Wastewaters containing dyes can be treated with Advanced Oxidation Process (AOP). AOP is an excellent technique to remove dyes from water and different industrial effluents [40–42]. Several metal oxides photocatalysts, specifically titanium dioxide (TiO_2), zinc oxide (ZnO), tungstate (WO_3), vanadate (VO_4), molybdate (MoO_4), and others [43–45] have demonstrated their potential in the degradation of dyes in wastewater. Among them, TiO_2 is mostly utilized due to its high photocatalytic activity, chemical stability, low toxicity, and economical cost [46]. TiO_2 photocatalysts generate OH• semi-permanently utilizing just photo-energy without extra synthetic chemicals, although the low radiant proficiency of TiO_2 is an limitation to its utilization in water treatment [47]. Heterogeneous photocatalysis utilizing metal oxides, for example, TiO_2, ZnO, $SnO_{2,}$ and $CeO_{2,}$ has demonstrated its proficiency in degrading a wide range of different pollutants into biodegradable compounds and, in the long run, mineralizing them to non-toxic carbon dioxide and water [14]. Recent research has also proved that (Fig. 4) metal oxides can be utilized as a photocatalyst to deteriorate toxic organic compounds, photovoltaics, prevent fogging of the glass, a promising self-cleaning, antibacterial, and even split water into hydrogen-oxygen. Consequently, they have significance in natural remediation, storage, hydrogen generation, and electronic industries [40,41,48,49]. The uses of such a photocatalytic process are specifically required for the decontamination of wastewater by removing microscopic organisms and different toxic compounds to make the water reusable.

4 TiO_2 as photocatalyst

TiO_2 is the favored catalyst for the photocatalytic treatment of dye wastewater. TiO_2 is utilized as a photocatalyst in dye wastewater treatment mainly because of its capacity to produce a high oxidizing electron-hole pair, great chemical stability, non-toxicity, and long-term photostability [38,40,48,50]. TiO_2 normally occurs in three common crystalline polymorphs: anatase, rutile, and brookite. The bandgap energy (Eg) of rutile and anatase is Eg = 3.0 eV and Eg = 3.2 eV, respectively [51].Although the anatase stage is considered the most photocatalytically active state, rutile is the most thermodynamically stable and is about 1.2– 2.8 kcal mol^{-1} more stable than anatase [40,52]. Also, the wide energy bandgap (Eg > 3.2 eV) in anatase may constrain its potential because just UV light with wavelengths under 387 nm can start the electron-hole separation process [50,53]. Consequently, it is an incredible challenge to obtain a good photocatalyst from TiO_2 that can productively utilize the energy from natural sunlight, comprising about 5% UV light and 45% visible light [50,54].

In 1972, Fujishima et al.[18] announced photo-induced decomposition of water on TiO_2 electrodes. Since Frank and Bard [55] first analyzed the chances of utilizing TiO_2 to deteriorate cyanide in water, there has been an expanding interest in ecological applications. Photocatalytic reactions at the surface of titanium dioxide have been drawing in much consideration in the perspective of their practical applications to environmental cleaning such as self cleaning of tiles, glasses, and windows. Titanium dioxide speaks to be a successful photocatalyst for water and air purification and self-cleaning surfaces. It may also be utilized as an antibacterial agent due to its vigorous oxidation activity and super hydrophilicity [15]. TiO_2 demonstrates high reactivity and chemical stability under ultraviolet light (λ<387nm), whose energy exceeds the bandgap of 3.3 eV in the anatase crystalline phase. The advancement of photocatalysts displaying high reactivity under visible light (λ> 400 nm) should permit the central part of the solar spectrum to be utilized. A few methodologies for TiO_2 modifications have been proposed: metal-ion implanted TiO_2 (utilizing transition metals: Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt), reduced TiO_2 photocatalysts [56,57], non-metal doped-TiO_2 (N, S, C, B, P, I, F) [58–60], composites of TiO_2 with semiconductor having lower bandgap energy (for example Cd-S particles[61], sensitizing of TiO_2 with dyes (for example thionine) [62] and TiO_2 doped with upconversion luminescence agent [63,64].

The photocatalytic mechanism starts when a photon hυ whose energy is equivalent to or greater than the bandgap of TiO_2 (~3.3 eV for the anatase stage) forming an electron-hole pair on the surface of TiO_2 nanoparticle as depicted in Figure 5. An electron is excited to the conduction band (CB), while a positive gap is created in the valence band (VB). The electrons and holes in the excited states with the ability to recombine, get trapped in metastable states, or react with electron donors and electron acceptors accumulated on the semiconductor surface or inside the surrounding electrical double layer of the charged particles. After reaction with water, these holes can create hydroxyl radicals with high redox oxidizing potential. Depending on the conditions, the holes, OH radicals, O^{2-}, H_2O_2, and O_2 itself, can participate in the photocatalytic mechanism [15,66].

In recent reports, it has been exhibited that the layered two-dimensional transition metal dichalcogenides (2D-TMDs), for example, molybdenum disulfide (MoS_2) based TiO_2 nanocomposite (TiO_2-MoS_2), can be a promising material for environmental applications [92–94].

4.1 Dopants

The addition (doping) of a suitable material to a catalyst can improve the efficiency of the photocatalytic process. Doping transition metal ions into the semiconductors leads to improvement of visible light photocatalysis [95]. A study showed that the doping of ZnO semiconductor, having tetrahedral O coordination of Zn, with transition metal ions (Cu, Co, Mn, and Fe) causes spin-exchange interactions resulting in the narrow bandgap, thus improving photocatalytic performance under visible light [96]. This change in the efficiency of the photoactivity was suggested because of the d-electronic configuration of the dopant and its energy level inside the TiO_2 cross-section [97]. Various metal and non-metal dopants such as vanadium, iron, rhodium, silver, sulfur, nitrogen, carbon, and fluorine have been used to enhance the photocatalytic efficiency of titanium dioxide [1].

It was suggested that the incorporation of a lower concentration of vanadium ions into the TiO_2 causes the absorption edge in the visible region, and thus, the improved photocatalytic action was observed. Whereas, excess of vanadium ions at higher concentrations mask the TiO_2 surface and provide recombination centers for electrons and holes in the excited state, resulting in a decrease in photoactivity in the visible light [98].

The synergetic effect caused by doping of some nonmetal ions [B, C, N, and S] into the TiO_2 also enhances the photocatalytic performance in visible light [99,100]. The higher photocatalytic performance observed in N doped ZnO as compared to pure ZnO was because the conductivity of the samples was conserved from zinc oxide to nitrogen, which resulted in redshift, thereby improving the photocatalytic performance under visible light irradiation [101]. In another study, the N-S co-doped TiO_2 catalyst was shown to have higher photocatalytic activity under visible, for the degradation of methyl orange, due to a high amount of oxygen vacancies [102].

The addition of transition metals to the TiO_2 structure has demonstrated to upgrade the photo-reactivity of the catalyst by behaving as traps for either electrons or holes, dependent upon the metal ion being electron acceptor or donor [103,104], corresponding to an n-dopant and p-dopant. Trapping of either of the charge carriers keeps it from recombining with the counter carrier. Thus, the outcome is an expansion in the lifetime of the electron-hole pairs, so it goes to the surface of the photocatalyst before recombination [105].

Doping titanium with transition metal ions helps in decreasing the bandgap for electron-hole pairing. There are two dopants, namely n-dopant [Cr3+] and p-dopant [Mo5+]. It was identified that the bandgap was shifted from 3.2eV (400nm) for pure titania to 2.85eV (435nm) with Mo doping and to 2.00eV (600nm) with Cr doping. By incorporating transition metal ions, new trapping sites are introduced, affecting the lifetime of the charge carriers. Doping reduces this lifetime to about 30 microseconds in the case of Cr^{3+} and about 20 microseconds with Mo^{5+} [106]. Due to the fivefold positive charge on the Mo surface, it increases the absorption level of dye onto the catalyst. Both adsorption and photo-degradation increases. Since there is a higher surface coverage of the dye, more charge carriers reaching the surface can contribute to the degradation process.

4.2 TiO_2-MoS_2 Photocatalyst

TiO_2 becomes active only under illumination with UV light (3-4% of the solar energy) due to its broad bandgap (3.2 eV), and the visible portion (around 45%) cannot be utilized successfully [107]. Therefore, the primary target is to decrease the bandgap of TiO_2 for making it photosensitive to visible light. The enhancement of optical absorption in the visible region will enhance the photocatalytic effectiveness of TiO_2, which may advance solar light use. In the most recent decade, extraordinary endeavors have been made to alter the bandgap of TiO_2. These results demonstrate that metal particle doping is one of the viable ways.

At present, the examinations about doping components, for the most part, center around transition metal particles doping [108–110]. Transition metal ions adjust micro-structures and electronic structures of TiO_2 and enhance its photocatalytic proficiency. Molybdenum (Mo) is a transition metal, and its doping into TiO_2 can move the absorption edge towards the visible region, increment the absorption under both UV and visible light, and improve the photocatalytic action of TiO_2. [111–114].

Novel preparations of the nano-MoS_2/TiO_2 composite have broad absorption in the visible spectra and exhibit efficient photocatalytic activity. The composites efficiency depended on the concentration of the dyes and the composite but was independent of pH and temperature. The photocatalytic activity was a consequence of photoelectron production and photo hole production, which are least affected by environmental temperature, which explains the ineffectiveness of temperature in the degradation rate of these dyes. The composites can be recovered by filtration and reactivated by warming in H_2. These composite could be potential photocatalytic materials for the expulsion of synthetic organic compounds from wastewater, for example, natural dyes and phenols. In addition, they may have potential applications in the hydro-desulfurization of unrefined petroleum and the synergist oxidation of S_2 [115].

A simple technique to synthesize hybrid MoS_2–TiO_2 nanomaterials at low temperatures with improved reactant properties with a critical potential for the photodegradation of organic compounds has been demonstrated [116]. MoS_2 nanoparticles anchored on the surface of anatase nanoparticles do not have a reductive impact on the bandgap vitality of the hybrid material. However, they are ready to expel electrons from the surface of anatase. The highest photocatalytic action for the degradation of Methylene blue (MB) was reached for the MoS_2– TiO_2 test containing 7.1 wt% of MoS_2.

Molybdenum disulfide (MoS_2) with a layered structure has attracted much consideration on photocatalytic water splitting for hydrogen creation inferable from its substance stability. Shen et al. [117] reported one dimensional (1D) MoS_2 nanosheet/porous TiO_2 nanowire (shell/center) crossover nanostructures synthesized by a hydrothermal strategy, prompting an enhanced particular surface region (66 m^2/g) in contrast to MoS_2 nanosheets (48 m^2/g). These 1D structures with the porous center as co-catalyst exhibited high action in the visible light photocatalytic hydrogen evolution response with an upgraded hydrogen generation rate.

TiO_2-MoS_2 heterostructure with a 3D hierarchical structure was reported for the first time employing the aqueous response by utilizing the TiO_2 nanobelts with the rough surface as the format [118]. The TiO_2-MoS_2 heterostructure showed excellent photocatalytic hydrogen generation when 50 wt% of MoS_2 was stacked on the TiO_2 nanobelts. Additionally, the TiO_2-MoS_2 heterostructure showed high level of adsorption and photocatalytic decay of organic dyes.

MoS_2 hybridization had an effect on the bandgap, interfacial electron transport, and response to visible light for the MoS_2/TiO_2 heterocomplex [119]. A redshift in the optical absorption edge and an improved activity under visible and UV light spectra was observed. The bandgap of the MoS_2/TiO_2 complex was found to be 1.6eV. Thus, they concluded that MoS2 could be an efficient sensitizer in the MoS2/TiO2 complex, and the photogenerated electron-hole sets are then very much isolated by the interface charge exchange will enhance the visible light photocatalytic movement of MoS_2/TiO_2 nanocomposite. Thus, the MoS_2/TiO_2 nanocomplex can be potentially used as a photocatalyst under visible light for the degradation of environmental pollutants.

MoS_2/TiO_2 heterostructure thin films prepared using sol-gel and substance bath deposition techniques demonstrated that covering ultra-thin MoS_2film onto the TiO_2-glass substrate improves photocatalytic activity under visible light [120]. The most effective photocatalytic performance under visible light, showing around 60% degradation of methylene blue in 150 minutes, was demonstrated by the MoS_2/TiO_2 heterostructure thin film having 45-minute MoS_2 layer deposition time.

N-doped TiO_2/MoS_2 (NTMS) heterojunction photocatalyst prepared by hydrothermal strategy, deomonstrated more grounded visible light assimilation and higher photodegradation activity than un-adulterated TiO_2, MoS_2, and NT (N-doped TiO_2) [121]. The arrangement of heterostructure between MoS_2 and NT was found to enhance visible light retention and significant charge transport and separation, resulting in improved photodegradation activity of MB. The NTMS catalysts showed high stability and therefore, could be applied for environmental remediation.

MoS_2 ends up being an admirable material for environmental applications because of its vast surface zone, solid surface adsorbability, and low cost [107]. Using MoS_2 as an intense scrounger, a few attempts have been made to investigate and improve the adsorption limit. Qiao et al. [122] detailed the hydrothermal formation of MoS_2 ultrathin nanosheets and showed that prepared MoS_2 displays removal of methylene blue from aqueous solution, with the most outstanding adsorption limit of 146.43 mg g^{-1}. Wang et al. [123] exhibited the MoS_2 nanoflowers with an adsorption limit of 49.2 mg g^{-1} on Rhodamine B. Massey et al. [124] revealed that color adsorption limit for methylene blue by various leveled microspheres of MoS_2 nanosheets was discovered to be 297 mg g$^{-1.}$. Song et al.[125] have incorporated Fe_3O_4/MoS_2 nanocomposite for the removal of Congo red from aqueous solution with an adsorption limit 71 mg g^{-1}. The adsorption limits of various dyes by the MoS_2 nanosheets and found that the MoS_2 nanosheets have higher adsorption capacities for Congo red (250 mg g$^{-1)}$ than for methylene blue (<100 mg g 1) [126]. MoS_2-rGO nanocomposites also demonstratesd higher adsorption capacity towards Congo red (440.9 mg g^{-1} at pH=3) than for methylene blue (<100 mg g 1) [127]. MoS_2 /graphene quantum dab nanocomposite (MoS_2/GQD) demonstrated ability to adsorb different natural dye [128]. MoS_2 microspheres produced using PEG under hydrothermal condition could effectively remove MB in aqueous solution [129]. But still, a great deal must be done to build up the MoS_2 based framework on the adsorption conduct for the technological viability.

MoS_2-TiO_2 nanocomposites for multitasking performance as nano-adsorbents and antibacterial agents have been developed [130]. This could remove methylene blue (maximum adsorption limit of 364.56 mg g^{-1}) and had the potential to act as antibacterial agent against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli.* The lactate dehydrogenase leakage assay (LDH) confirmed the reliable connections between the nanocomposite and the surface of the cell film causing rupture of bacterial cell membranes at the same time the biocompatibility test against human blood cells demonstrated the nontoxic impact. Overall, the MoS_2-TiO_2 nanocomposites, with synergistic performance, are a potential multifunctional material to address environmental and health issues.

Various studies have also shown the reusability and stability of photocatalysts like ZnO, Zr co-doped Ag-ZnO, and CeO_2-reduced graphene oxide (CeO_2/RGO) nanocomposites [131–133]. Photocatalysts based on zinc oxide (ZnO) have been prepared using three methods: i.e., electrolysis, hydrogen peroxide, and heat treatment. The photocatalytic degradation of MB was obtained up to 84%, 79%, and 65% within one hour for ZnO layers synthesized by electrolysis, heat, and hydrogen peroxide treatment, respectively [131]. Additional reaction time was required by the samples to reach the maximum degradation of methylene blue in subsequent cycles and these varied with the preparation method. The half-life of the ZnO layer synthesized by electrolysis, heat, and hydrogen peroxide treatment was found up to the sixth, fifth and third cycles, respectively [131].

Zr co-doped Ag-ZnO photocatalysts with different wt.% of Zr by precipitation–thermal decomposition method. Zr-Ag-ZnO showed complete degradation of anionic azo dye Reactive Red 120 (RR 120) within 30 min of treatment and demonstrated reusability with a slight drop in efficiency from 100% (1st run) to 96.0 % (4th run) [132]. CeO_2-reduced graphene oxide (CeO_2/RGO) nanocomposites (2:1 ratio of CeO_2 to RGO) produced by a one-step hydrothermal reaction using cetyl trimethyl ammonium bromide (CTAB) as a surfactant, demonstrated 88.3% photocatalytic removal of methyl orange compared to the bare CeO_2 catalyst and also had good reusability [133].

4.3 Photocatalytic reactors

The current focus is on the Reactor configuration for photocatalytic water treatment. The reported photocatalytic reactors can be grouped into two classes, i.e., (i) lab-scale reactors, with rector volume <1 L, and (ii) pilot plant-scale reactors, with >5 L reactor volume [1]. In the ongoing developments of lab-scale reactors, various UV/Visible LEDs (Light Emitting Diodes), which require less energy, are being utilized as light sources. Other development in the reactor designs at lab scale involves using immobilized catalytic beds, rotation disc type reactor models, and reuse of catalyst powder separated after each treatment cycle. LED's are light sources that need less energy and, in this way, LED-based photocatalytic reactors are more energy proficient frameworks (Figure 6). The blend of UV-LED's and NTO powder [134] NTO nanotubes [135], or immobilized NTO [136,137] has been used for the degradation of different dyes, for example, methyl orange, rhodamine B, malachite green, and Methylene blue. Nickels et al. [136] successfully created a UV-LED photoreactor for demonstration of methyl orange dye degradation. It was fitted with a microcirculation fluid pump and had an in-stream sensor unit (Figure 4). This reactor proved to be ideal for lab-scale as well as pilot-scale applications due to its cost-effectiveness, adaptability, and less weight.

Vilar et al. [138] and Pereira et al. [139] used a Compound parabolic collector pilot plant for the treatment of Cork boiling and bleaching wastewater and Oxytetracycline, respectively, using TiO_2. It was used for a volume of 22 and 110 L. Remoundaki et al. [140] tested the photolytic and photocatalytic effect on the humic substances in a solar concentric parabolic concentrator (CPC) reactor. This reactor was used for a volume of 16.2L. Benotti et al. [141] tested the Membrane pilot system for the photocatalytic treatment of pharmaceuticals and endocrine disruptors from wastewater. Various other researches, such as that done by Zayani et al. [142] and Vargas et al. [143], used thin-film fixed- bed reactor and Tubular continuous flow pilot plant reactor for their photocatalytic studies on azo dyes and hydrocarbons.

The outline of photocatalytic reactors is a crucial zone where exceptional research is in advancement. A perfect photocatalytic reactor ought to be straightforward, vitality productive, more affordable to fabricate and work, and ready to deal with high wastewater volumes. Reactors working with sun-powered radiation or LED and reactor plants that do not require post-partition of the catalyst hold incredible guarantee.

5 Industrial Dyes as pollutants

Colorants, or addictive substances resulting in light absorption at different wavelengths, can be classified as pigments and dyes. Dyes are solvent or somewhat soluble natural (carbon-based; plant and creature extricated) colored compounds suspended in a medium [144]. The process of applying color to textile fibers is known as dying. In contrast, pigments are insoluble and do not show any chemical affinity for the substrate to be colored [16].

Dyes can be of different types such as acid, basic, direct, disperse, reactive, anionic, cationic, and so forth. Of the synthetic dyes manufactured today, azo compounds are overwhelming (~50– 70%), with anthraquinone colors being the second [16].

The residual dyes from various sources (e.g., textile industries, paper, and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft blanching industries, and so on) are viewed as potential organic pollutants entering into the water resources or wastewater treatment systems. One of the principal sources with serious contamination issues worldwide is the textile industry and its dye rich wastewaters (for example, 10,000 different textile dyes having an expected yearly generation of 7.105 metric tons are economically accessible worldwide) [145–147]. The dyeing process in textile industries releases approximately 10-25% of dyes, and 2-20% is released directly as effluents in various ecological components [148]. Specifically, the release of dye-containing effluents into the aquatic environment is unwanted due to their color, as well as the breakdown products of a large number of dyes that can be highly hazardous to aquatic life forms; many of the breakdown products such as naphthalene, benzidine, and other aromatic compounds can be responsible for causing cancer, mutations, etc.,[149,150]. Without sufficient treatment, these dyes can stay in the environment for an extended time. For example, the half-existence of hydrolyzed Reactive Blue 19 is around 46 years at pH 7 and 25°C [151].

5.1 TiO_2 used in the treatment of different dyes

A description of TiO_2-assisted photocatalytic degradation of organic dyes has been explained in various research articles (Tables 2). Around 50– 70% of the dyes accessible in the market are azo compounds and anthraquinone compounds [153]. Some azo dyes and their dye antecedents have been accounted for as human carcinogens in many pieces of research [11,154–156]. Thus, azo dyes are poisons causing serious environmental damage and were chosen as the most influential group of dyes concerning their degradation utilizing TiO_2 mediated photocatalysis. Azo dyes can be separated into monoazo, diazo and triazo classes as indicated by the presence of at least one azo bond (– N N–). Azo dyes are found in different classifications, including acid, basic, direct, disperse, azoic, and pigments (Table 3). Table 6 describes the structure and properties of different azo dyes that have been the subject of TiO_2-assisted photocatalysis colors, having additional genuine ecological effects. Other organic dyes such as indigoid, anthraquinone, triarylmethane, and xanthenes dyes also pose a high environmental risk and may be used in photocatalytic processes.

Mainly, the sites near the chromophore (for example, C– N, −N N– bond) are the targeted region in the photocatalytic corruption process. Photocatalytic rupture of the C– N and –N N– bonds results in fading of the dyes. As indicated in various literature, both UV light and a photocatalyst, for example, $TiO_{2,}$ are required for the proper degradation of these organic dyes [157–160]. For example, the process of photocatalysis (UV/TiO_2) and photolysis (UV alone) in the degradation of Direct Red 23 were compared. The presence of both TiO_2 and UV light resulted in removing 54% of the dye at the illumination time of 180 min. This was high compared to the ~2% degradation for a similar analysis performed with the photolysis process [161].

5.2 Toxic intermediates of dye degradation

A significant number of the dyes utilized in different industries are lethal and carcinogenic, resulting in exposure to aquatic life forms [195]. Because of the toxicity and adverse impacts of dyes discharged to the environment through wastewater, its degradation processes have been extensively studied.

Azo dyes are compounds containing at least one or more azo groups (- N=N-), connected to phenyl and naphthyl radicals, which are typically substituted with a few combinations of functional groups including amino (- NH_2), chlorine (- Cl), hydroxyl (- OH), methyl (- CH_3), nitro (- NO_2), sulphonic acid and sodium salts (- SO_3Na) [195]. Azo dyes, obtained from aromatic compounds, are not basic in aqueous solution (because of the presence of the N=N linkage, which decreases the likelihood of unpaired electron pairs in nitrogen molecules), are reduced to hydrazines and essential amines, working as great oxidizing agents[196]. The presence of dyes in the aquatic environment results in an aesthetic problem and can negatively affect human health. It was proved that azo dyes, after cleavage, present the ability to discharge carcinogenic aromatic amines. The European Union, by the Directive 2002/61/EC, reformulated by the Directive 2004/21/CE, has prohibited the utilization of these dyes in the production of textile articles that comes in contact with skin or mouth. These directives additionally state that the mentioned textile articles can not contain the 22 amines mentioned in the legislation at a concentration higher than 30 ppm and, if the articles are produced from the recycled fibers, they should not contain more than 70 ppm [197]. Some substances obtained from the dyes have been examined, in laboratory animals, to determine the toxic impacts of these compounds on living organisms.

Evaluation of the toxicity of azo dyes and metabolites derived from their degradation is vital for the development of methods to decrease the harmful effects of these chemicals [198,199]. Some azo dyes possibly display mutagenic activity when the azo bond is reduced. Depending upon the chemical structure, the aromatic amines formed can be more or less carcinogenic or mutagenic, as compared to the original compound. As indicated by Plumb et al. [200] and Yoo et al. [201], these aromatic amines are more toxic as compared to the original compound and may have toxic, mutagenic, and carcinogenic activities. The reduction of these azo dyes can create DNA adducts, resulting in dangerous impacts, including the microorganisms that participate in the discoloration of azo dyes [202–208].

Degradation of dyes occurs by anaerobic microorganisms by reducing their nitrogen bonds, which causes the production of toxic, carcinogenic compounds due to the biological degradation [11,209,210]; however, one can recover the color by bringing oxygen in contact with the anaerobic degradation products [211]. These problems greatly restrict the use of bacteria for color removal. Photocatalysis emerging as new wastewater treatment technology is an Advanced Oxidation Process, which can be utilized to mineralize toxic colored compounds discharged from textile and other industries. Among all semiconductor materials being researched upon, TiO_2 has been become the preferable semiconductor material because of the mild conditions required for the synthesis and its high photocatalytic activity, causing the mineralization of toxic dye compounds and can be effectively used to bring about new developments in the dye rich wastewater treatment. Additionally , it also is known to oxidize the more significant part of the organic contaminants to CO_2 and H_2O [212,213].

Based on the number of reactive groups present in the dye compound, the reactive groups can be classified as mono-, bi- and polyfunctional reactive structure. The particular dye properties can be easily achieved by altering the dye molecular structure [152].

The toxicity of some dyes and intermediates has been recognized for some time. Acute or short-term impacts are commonly known. They are controlled by keeping the concentration of the chemicals in the work environment under the recommended levels and preventing physical contact with the material. On the other hand, chronic effects generally appear only after a long period of exposure. It has been determined statistically that higher frequencies of benign and malignant tumors, particularly in the bladders of workers exposed to specific intermediates and dyes, were recorded in dye producing nations during the period 1930– 1960. The specific compounds included were 2-naphthylamine, 4-aminobiphenyl, benzidine (4,40-diaminobiphenyl), fuchsine (CI Basic Violet 14), auramine (CI Solvent Yellow 2). There is ample proof that metabolites of these compounds are genuine carcinogenic [214,215]. Strict controls concerning the treatment of known carcinogenic agents have been forced in most industrial countries. Other genuine or suspected carcinogens, for example, the nitrosamines, or N-nitroso mixes, polycyclic hydrocarbons, alkylating specialists, and other individual compounds, for example, the dichromates, should be included in the broader context of industrial chemistry rather than as dye intermediates [216]

Three mechanisms of azo dye carcinogenicity were distinguished, including metabolic activation to reactive electrophilic intermediates that covalently bind DNA. These mechanisms [11] are described as:

1. Azo dyes that are harmful only after reduction and cleavage of the azo linkage giving aromatic amines, generally through intestinal anaerobic bacteria. Azo dyes work as a vehicle for the component, perhaps toxic, aromatic amines. Studies on structure-activity depict that reducing azo to free aromatic amines by liver proteins or by intestinal anaerobic bacteria is reasonably dependent on electronic and steric effects; however, any azo compound can be reduced in vivo. The toxicity of azo dyes can thus be anticipated depending on the toxicity of component amines. The aromatic amine toxicity has been built up to include oxidation of the nitrogen atom, with or without prior formation of an N-acetyl or N-glucuronide metabolite, to form highly electrophilic species that can covalently bind to DNA.
2. Azo dyes with structures containing free aromatic amine groups that can be metabolically oxidized without azo reduction. Some azo compounds with aromatic mono-or dimethylamine groups are metabolically de-alkylated to create the free aromatic amine. An azo reduction that is not required for this mechanism may even be a detoxication reaction in these cases.
3. The third mechanism is the direct oxidation of the azo bond to diazonium salts, which are highly reactive and electrophilic imparting carcinogenicity to the azo dyes.

Benzidine is a known bladder carcinogen in people, and 3,3'-dimethyl, - dimethoxy, and - dichloro benzidines are carcinogenic in laboratory animals and are probably going to be human cancer-causing agents as well [217]. Benzidine and substituted benzidines are structural components of numerous azo dyes known as carcinogens in both laboratory animals and humans [218]. Benzidine might be available in technical dye samples as a contaminant from the incomplete azo coupling or by compound reduction during the storage of dyes. Azo dyes might be photochemically azo reduced to the respective aromatic amines. As a result, the illumination of the azo dyes, Carmoisine and Ponceau 4R (= Ponceau MX) with a source of simulated sunlight produced 1-amino naphthalene, a carcinogen both in humans and laboratory animals [218].

As many of the azo dye causes toxicity after their reduction to aromatic amines, evaluation of the toxicity of the component aromatic amines is essential [11].

5.3. Toxicity of Titanium dioxide nanoparticles

Large scale use of nanomaterials in various applications presents an excellent potential for human exposure and ecological discharge. The reactivity of the materials changes as they enter the nanoscale range. Subject to their small size, nanoparticles possess a large surface area to volume ratio and exhibit excellent physical and chemical properties unique from their traditional forms [219].

Various factors like size, aggregation, composition, crystallinity, surface area, etc., are responsible for altering the toxic behavior of nanoparticles. Also, the small sizes of the nanoparticles enable them to translocate in the body and reach the circulatory and lymphatic systems and finally enter the organs. Some nanoparticles have the capability to cause severe damage to the cells by causing oxidative stress or may result in organelle damage, depending on their size and composition [220].

Food and Drug Administration (FDA) has approved the use of TiO_2 in food additives since 1996 at a lethal dose, at 50% concentration (LD50), of greater than 10 g/kg [221]. 50 μg/kg body weight/day of nano-TiO_2 (nTiO_2) has been defined as safe dose for humans by the FDA and Environmental Protection Agency (EPA) (Title 21, volume 1, revised as of April 1, 2014). Moreover, the daily intake of nano- TiO_2 in general foodstuffs have been approved by the European Commission's Scientific Committee on Food (SCF), the Joint Expert Committee on Food Additives of the Food and Agriculture Organization/World Health Organization (JECFA), and the European Food Safety Authority (EFSA) 's Scientific Panel on Food Additives, Flavorings, Processing Aids and Materials in Contact with Food. In terms of adverse health effects, various experimental and epidemiological data have evaluated TiO_2 as biologically inactive and physiologically inert, showing low toxicity, thus producing low risk to humans [222]. TiO_2 did not show any absorption or tissue accumulation in the studies done by JECFA and EFSA; also, there have not been any health hazards for occupational workers and public health by Material Safety Data Sheets (MSDS) [223]. Apart from these reports, the World Health Organization (WHO) 's Environmental Health states that "titanium compounds are poorly absorbed from the gastrointestinal tract, which is the main route of exposure for the general population" (WHO 1982) (Figure 7). They present low toxicity potential in mammals or aquatic species *(Daphnia magna, Oncorhynchus mykiss)*[224]. Although the above data shows TiO_2 to be nonhazardous to life forms and non-toxic to the biological environment, contrasting results have been described by the Scientific Committee on Consumer Safety (SCCS).The have detailed the genotoxic, carcinogenic, and photosensitization behavior of TiO_2 NPs and many adverse effects of TiO_2 NPs have been shown in several in vitro and in vivo studies on biological systems [225,226]. Yin et al. [223] have shown that the phytotoxicity of TiO_2 NPs under UV irradiations is caused by all the molecular sizes and crystal forms (anatase and rutile) of TiO_2 . The acute toxicity of TiO_2 has also been reported in mice at different dosages of 0, 324, 648, 972, 1296, 1944, or 2592 mg/kg body weight [227]. Various researches have reported that the generation of Reactive Oxygen Species (ROS) may result in inhibition of the heat shock proteins (HSP) [228,229], up-regulation of the inflammatory cytokines and apoptosis-related genes[221,230,231], and cause neuroinflammation [232]. Park et al. [228] and Shi et al. [233] have descried that the small size (10–20 nm) TiO_2 NPs have the potential to induce oxidative DNA damage, lipid peroxidation, and increased hydrogen peroxide (H_2O_2) and nitric oxide production in BEAS-2B cells (human bronchial epithelial cell line) without photoactivation.

For a long time, TiO_2 has been known as "the knight" due to its limited toxicity [234], inertness, and biocompatibility [221,223]. However, when it enters the nanoscale range, the surface area per mass increases linearly, resulting in an increase in the reactivity. Higher reactivity brings about a change in their toxicity properties and also affects their associations with living organisms. Due to the smaller size, these nanoparticles can reach the areas that are inaccessible by the bulk particles, resulting in their accumulation. Various studies have reported the cause for TiO_2 NPs toxicity to be the formation of reactive oxygen species (ROS) on UV irradiation, resulting in damage to the cellular and subcellular structures [235,236].

As the nanoparticles exhibit size close to that of cellular components and proteins, they have the potential to travel inside the human body [237]. Some studies have also reported the penetration of nanoparticles into the skin [238,239]. TiO_2 nanoparticles have been suggested to cause DNA and pulmonary damages [240]. An increase in the IL-8 levels was observed on the exposure of TiO_2 nanoparticles to human endothelial cells [241]. Overall, the present studies done on mice suggest that nanoparticles have the ability to induce the production of reactive oxygen species (ROS), oxidative stress (OS), and inflation in the vasculature and lungs [242,243]. It has been known that oxidative stress is the primary origin of ROS, which includes the superoxide anion ($O\cdot^{-2}$), hydrogen peroxide (H_2O_2), hydroxyl radicals ($\cdot OH$), and peroxynitrites [244]. This would further result in cell death due to oxidative DNA damage and increased level of cellular nitric oxide [237,245,246]. The oxidative stress-mediated toxicity of nano-TiO_2 has been reported in many cell types such as liver, skin fibroblast, endothelia, epithelia, Salmonella bacteria, and alveolar macrophages [247–253]. Their toxicity to fish cells in vitro and algae has also been suggested [254,255].

Since the application of metal oxide nanoparticles has increased tremendously in various applications; thus, they present a possible release of toxic heavy metals into the environment [256]. Some metal oxides react with light and can act as photosensitizers, and some can be used as semiconductors [257]. Metal oxide photocatalysts have found a great deal of application in the textile industries for the treatment of wastewater containing dyes, as discussed above. Exposure of the photoreactive nanoparticles present in the aqueous environment often results in changes in their toxicity characteristics. This calls for a great need to investigate into the ways in which the light at different wavelengths can alter the toxicity of light-absorbing nanoparticles. ZnO and TiO_2 nanoparticles have found their use in various products and applications such as sunscreen, cosmetics[258], toothpaste, and textile[259]. Various scientists have reported the effects of these nanoparticles in aquatic species such as fish [224,260–262], water flea [224,260,263–267], and algae [224,254,263,268–274]. The toxicity of ZnO nanoparticles on freshwater green algae (*Pseudokirchneriella subcapitata*) and marine diatom (*Thalassiosira pseudonana*) have been tested by Franklin et al. [268], Aruoja et al. [254], and Miao et al. [275]. Miller et al. [273] has reported the phototoxicity of TiO_2 NPs on marine phytoplankton (*Thalassiosira pseudonanan, Skeletonema marinoi, Isochrysis galbabana*, and *Dunaliella tertiolecta*).

Subjected to the wide application, titanium dioxide nanoparticles tend to leak into the marine environment through urban activities, surface runoff, sewage and waste discharge, and marine structure coatings [276]. It was suggested that organisms in the lower and higher trophic levels are primarily affected [277].

Marine zooplankton is an essential part of the marine food chain and highly susceptible to these nanoparticles. These zooplanktons obtain food particles of size diameter less than 50μm from water [263,278]. As a result, they can mediate the transfer of various pollutants and nanoparticles to higher trophic levels [266].

Bhuvaneshwari et al. [279] evaluated toxicity and transfer potential of TiO_2 nanoparticles in the trophic levels from marine algae *Dunakiella salina* to marine crustacean *Artima salina*. However, in their study, they did not find any trophic transfer from algae to *Artima* through dietary exposure concluding a lack of transfer potential of TiO_2 nanoparticles.

Apart from this, the marine environment is also rich in various contaminants, including polycyclic aromatic hydrocarbons (PAHs) and metal ions (Cd^{2+}, As^{3+}, and Pb^{2+}). The high surface area of TiO_2 nanoparticles enables them to absorb these contaminants and form complexes that are toxic to the aquatic environment [280]. Tian et al. [281] reported that TiO_2 nanoparticles might act as carriers, resulting in phenanthrene bioaccumulation in marine ark shells.

It has been shown that TiO_2 nanoparticles enhance the bioaccumulation and toxicity of Pb, Cu, As(II), Zn, and Cd in zebrafish larvae, *Daphnia magna*, and *Cyprinus carpio* [9,275,282–284]. TiO_2 nanoparticles have shown conflicting results where it has shown to reduce the bioavailability and toxicity of Cd and Cu in alga (*Chlamydomonas reinhardtii* and *Microcystis aeruginosa*) and amphipod (*Gammarus fossarum*) [285–287] and has been reported to eliminate the toxicity of As(V) on *Ceridophnia dubia* depending on the TiO_2 nanoparticles to As ratio [288]. These results show that the effect of nanoparticles depends on the species-specific interactions between TiO_2 nanoparticles and heavy metals.

As reported by Wang et al. [289], the sedimentation of TiO_2 nanoparticles affected the vertical distribution of heavy metals through adsorption. In his study, TiO_2 nanoparticles increased the bioaccumulation and reproductive toxicity of Cd, As, and Ni to *Caenorhabditis elegans* dependent on the dose and size of TiO_2 nanoparticles. Also, the effect on the accumulation of As was lower than the other two.

Thus, we can say that TiO_2-NPs cause certain toxic effects reported in many studies, including inflammation, cytotoxicity, photo-toxicity, and genomic instability in mammals, plants, and microorganisms [259,290–294]. Also, TiO_2-NPs may pose significant risks to aquatic organisms [295,296]. With large-scale use of TiO_2 NPs, they are often found in wastewater and effluents resulting in their release to the aquatic environment, such as coastal areas. Till now, only limited studies on the ecotoxicological behavior of TiO_2-NPs have been done, where they have reported few studies on aquatic organisms. Federici *et al*. [297] studied the toxicity of TiO_2-NPs in rainbow trout (*Oncorhynchus mykiss*) and reported that TiO_2 NPs causes respiratory distress and sub-lethal toxicity involving oxidative stress, organ pathologies, and the induction of antioxidant defense system such as glutathione (GSH). However, he did not report any mortality effect on rainbow trout. Lovern and Klaper [298] have studied the toxicity of TiO_2 NPs on *Daphnia magna*, where they reported 100% mortality at 10 mg/L TiO_2 NPs concentration, concluding that with increasing nanoparticles concentration, the mortality rates also increases. However, sonicated TiO_2-NPs caused only 9% mortality with 500 mg/L TiO_2 NPs concentration tested for 48h. Zhu *et al*. [299] studied the toxicity of several metal oxide nanoparticles on zebrafish (*Danio rerio*) and concluded that both TiO_2 NPs and the bulk TiO_2 do not cause any toxicity to zebra fish embryos and larvae. It was also shown by Reeves *et al*. [255], that the TiO_2-NPs caused cytotoxicity and DNA damage in goldfish skin cells (GFSk-S1) which they concluded to be the result of hydroxyl radical ($^{\bullet}OH$) formation. However, the complete information on toxicological effects of TiO_2-NPs on aquatic organisms is limited.

Although present research indicates low acute toxicity caused by TiO2 NPs to fish, various sub-lethal effects of TiO_2 NPs have been reported in a few studies. For example, Federici et al. [297] and Hao et al. [300] reported histopathological changes in gills of rainbow trout and carp, respectively. Also, TiO_2 NPs may result in oxidative stress in various fish tissues, including the brain [297,300,301]. The neurotoxicity of TiO_2 NPs, causing oxidative stress and biochemical disturbances in the brain, raises the concern and need for toxicity studies on TiO_2 NPs. Many in vitro and in vivo studies have reported the brain to be the target organ for nanoparticles [302]. Long et al. [244,303] have reported that TiO_2 NPs produce reactive oxygen species (ROS) in brain microglia and damage neurons in vitro. Nanoparticles may be taken up by the nerve endings of the olfactory bulb and translocated to the brain in live fishes [304].

Moreover, after absorption into the blood by gills, the nanoparticles may also cross the blood-brain barrier and reach the brain via systemic distribution [295,302]. Hu and Gao [302] suggested that nanoparticles that reach the brain can be phagocytosed by microglia and accompanied by the formation of reactive oxygen species (ROS), which results in oxidative stress ensuing neurotoxicity. The oxidative stress caused by ROS has also been found to be the cause of many neurodegenerative diseases, Parkinson's disease, Alzheimer's disease, and Huntington's disease [305].

Various toxicological studies have also been done on plants [306–310]. All these studies did not report any kind of toxicity impacts in plants for TiO_2 nanoparticles. Servin et al. [311] reported that TiO_2 caused increased chlorophyll content and catalase activity in cucumber plant leaves. Song et al. [312]concluded that TiO_2 does not show any phytotoxicity in tomato plants, even at 500mg/kg. Feizi et al.[313] checked dose-dependent changes in seed germination and seedling growth in wheat seeds and did not report any type of changes on seeds exposed to TiO_2 nanoparticles.

Another primary concern in the ecotoxicity context is the organisms exposed simultaneously to light and photochemically active nanoparticles (e.g., TiO_2, ZnO, SiO_2, and fullerenes). These nanoparticles generate excited electrons when exposed to light, and in the presence of oxygen, they have the potential to form superoxide radicals by direct electron transfer [314].

Although the experiments on the acute ecotoxicity of TiO_2 NPs in crustaceans, fish, and algae present a low toxic ability of TiO_2 NPs for aquatic species, when they were subjected to chronic TiO_2 NPs induced many adverse effects. Additionally, nano-sized TiO_2 have the ability to enter into the freshwater food chain, resulting in their transfer from lower to higher trophic organisms, including humans [332].

Thus, based on the above information, it can be concluded that there is no clear evidence regarding the safe dose of TiO2 nanoparticles and great care has to be taken while working with these materials [333].

Few in vitro and in vivo studies on animals and cell cultures have shown some reproductive and developmental toxicities. However, it is still unclear regarding the reproductive and developmental toxicities on humans. Various animal studies show that continuous exposure to the nanoparticles may result in the accumulation of TiO_2 NPs in organs or tissues.

Although the toxicity of the nano-TiO_2 is not yet apparent, we have to take various steps to prevent their massive scale release into the freshwater bodies. One suggested way to reduce the exposure of humans and aquatic life forms to these nanoparticles may be the immobilization into various forms such as nanowires, matrix, etc., Immobilization of nanoparticles may be necessary due to the following reasons :

(i) Improve the safety of the material by immobilization of nanoparticles in the matrix (due to their potential of causing human toxicity).

(ii) It also allows easy handling of metal nanoparticles and simplifies their final application [334]

Conclusion

Various researches have shown the successful use of TiO_2 nanoparticles (anatase phase) in dye water treatment. Photocatalysis can be seen as an efficient method in treating effluents discharged from textile dying industries and various other industries. The bandgap of TiO_2 has been reduced by doping them with various transition metal ions and also by preparing heterojunction (combining them with different semiconductors), enabling them to be utilized in the visible light. Even after treatment, the azo dye compounds may form intermediates that pose a higher risk than the parent compound. The toxicities of various azo compounds and their intermediated have been discussed here. It has also been shown that TiO_2 may also pose various health risks and may even cause toxicities to the aquatic life forms. As indicated in many research pieces, TiO_2 nanoparticles have shown to cause inflammation, cytotoxicity, phytotoxicity, and genomic instability in mammals, plants, and microorganisms. The toxicity caused by TiO_2 nanoparticles accounts to the formation of reactive oxygen species (ROS), resulting in oxidative stress. However, only limited data is available regarding their toxicity on the fishes where they have been shown to cause only limited toxicity and do not result in mortality. TiO_2 nanoparticles may also affect the toxicity caused by heavy metals and may enhance their accumulation in the fishes. Since the results are still conflicting regarding the toxicity of TiO_2 nanoparticles, there is still a need to focus and study more about the potential ecotoxicity of these nanoparticles.

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