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A Brief Review of Transition Metal Doped TiO_2 Nanoparticles for Dye-Contaminated Wastewater Treatment

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Abstract: ***Transition metal-doped TiO_2 nanoparticles have gained significant interest for their enhanced photocatalytic performance in degrading dyes from contaminated wastewater. Doping with transition metals like Fe, Cu, Mn, Sr, and Zn modifies the electronic and optical properties of TiO_2 reducing its bandgap and improving its light absorption into the visible spectrum. This review explores the impact on photocatalytic efficiency of TiO_2 nanoparticles focusing on factors such as charge carrier separation, surface activity, and dye degradation rates when transition metal doping is done with TiO_2 nanoparticles. The review emphasizes the potential of transition metal doped TiO_2 nanoparticles as economical and ecofriendly materials for treating dye-contaminated water, supporting sustainable wastewater management methods.***

Keywords: transition metal, nanoparticles, photocatalytic, bandgap, wastewater, sustainable

1. Introduction

In the past few decades, ecological contamination has become a major issue due to the burning of fossil fuels, increasing industrial activities, global warming, agricultural activities, mining activities, domestic sources, construction & demolition, storm drains, urban runoff, industrial waste, radioactive contamination, and many other activities occurring regularly. As human civilization evolved, its growth has impacted nature in many ways; water pollution is the introduction of harmful substances into water bodies and underground water sources. This contamination compromises the quality of the water, rendering it unsafe for use and threatening the health of aquatic ecosystems, humans, and the environment as a whole. It is a pressing global issue that stems from various sources and has far-reaching consequences. Every day, a wide range of potentially dangerous chemicals are utilized, moved, and managed across multiple settings, from households to industrial operations. During these activities, accidents such as spills can happen, releasing pollutants and contaminating surface water or groundwater through direct or indirect means. [1]

Water pollution and organic dyes

Organic pollutants are gathering significant attention due to their extensive use and subsequent release into aquatic and terrestrial ecosystems. These substances are highly persistent, resistant to degradation, and can have adverse impacts on human health and the ecosystem. These tenacious organic pollutants are particularly concerning because they are challenging to break down and can pose various health risks, including cancer, congenital disorders, compromised immunity and progenitive ailments, and impaired development of babies and children. Such pollutants include a variety of substances like dyes, pesticides, pharmaceuticals, phenolic compounds, fertilizers, hydrocarbons, and plasticizers. [2] Water pollution from dyes is a major environmental issue, stemming from the discharge of coloured substances used in industries such as textiles, paper, leather, and dye manufacturing. The discovery of mauveine by William Perkin in 1865 marked the beginning of synthetic organic dyes, transforming the dye industry and leading to the widespread production of these materials globally. [3] By the early 20th century, Europe dominated the global dye production market. However, today, China and India have emerged as key players, major dye producers, and leading fabric suppliers, significantly shifting the industry's landscape away from traditional European dominance. [4] If not managed properly, these dyes can result in serious ecological and health issues. Over ten thousand colouring substances are being used in various industrial applications, with global manufacturing of man-made dyestuffsurpassing$7x10^8$ kg each year. [5] There is increasing awareness of artificial organic dyes as pollutants in water systems. These vibrant pigments find use across many sectors, including textiles, tanneries, cosmetics, food processing, and pharmaceuticals for both human and animal consumption. [6] Due to their widespread application and mass production, synthetic organic dyes have contaminated various environmental components, including aquatic resources, air, land, and aquatic food. Consequently, they are categorized as micropollutants in aquatic ecosystems. [7] Figure 1 represents the types of dyes produced by pharmaceutical industries, textile industries, food industries, leather industries, paints & varnishing industries, and households that cause environmental pollution affecting human health and aquatic life. [8] Many dyes fall into a harmful category of water pollutants, significantly affecting ecosystems. Certain dyes, such as methylene blue, rhodamine B, methyl violet, methyl orange, remazol brilliant blue, Congo red, and crystal violet, pose toxicity risks to humans. [9]

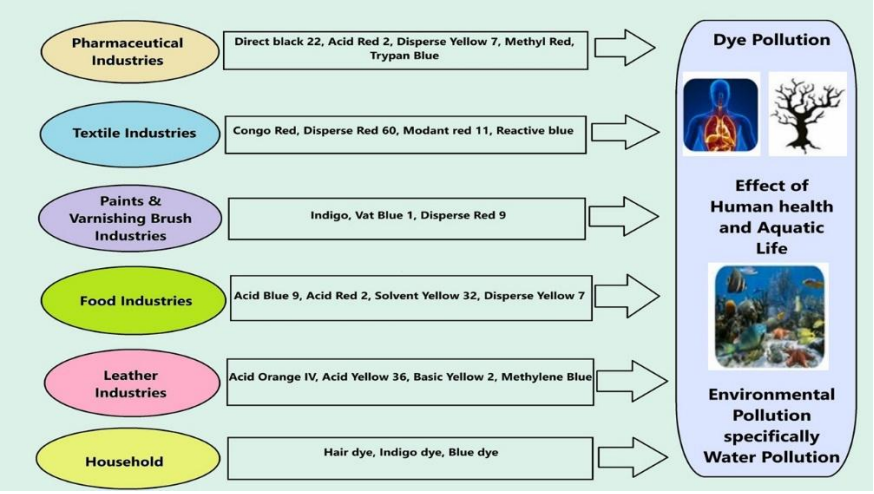

Figure 1: A schematic diagram representing the various dyes produced that cause water pollution [8].

Challenges in wastewater treatment

The elimination of organic pollutants from wastewater poses a significant challenge. Various endeavours have been undertaken to eliminate or break down organic contaminants in water. Different methods including physical separation, chemical degradation, and biological decomposition are used to remove dye contaminants from the wastewater either separately or together. Water can be purified through various techniques such as using adsorbents, filtering with membranes, biological treatment, photocatalysis, liquid extraction, nanofilters, chemical oxidation, reverse osmosis, UV light treatment, and several other processes. [10-12] Figure 2 represents a schematic view of water pollution caused by dyes and their treatment by various approaches including a photocatalytic approach for making water clean. [13] In the case of dyes, besides their unpleasant physical characteristics and toxicity, the continuously escalating production of dyes resulting from increased industrialization has made it imperative to find effective treatment methods. [14, 15] Hence, to address these evident and formidable effluents, numerous technologies have been explored to mitigate their potentially amplified environmental effects. Conventional physical methods are viable for dye removal. However, those techniques essentially transfer pollutants, leading to pollution to another medium. This typically necessitates additional treatment of solid waste and refilling of absorbing materials, thereby increasing the overall cost of the process. [16] There is an urgent need to develop modified nanomaterials and hybrid nano-based frameworks to address wastewater treatment challenges. However, there are significant hurdles to overcome, including high costs, technical limitations, and potential risks to human health and the environment. Collaborative research involving governments, research institutions, industries, and investors is essential to tackle these challenges. By addressing these issues, we can align with the principles of green and sustainable chemistry. Continuous development of nanotechnology-based water treatment solutions is necessary to provide effective strategies for water management. In the future, nanomaterials are anticipated to play a key role in environmental remediation and wastewater treatment.

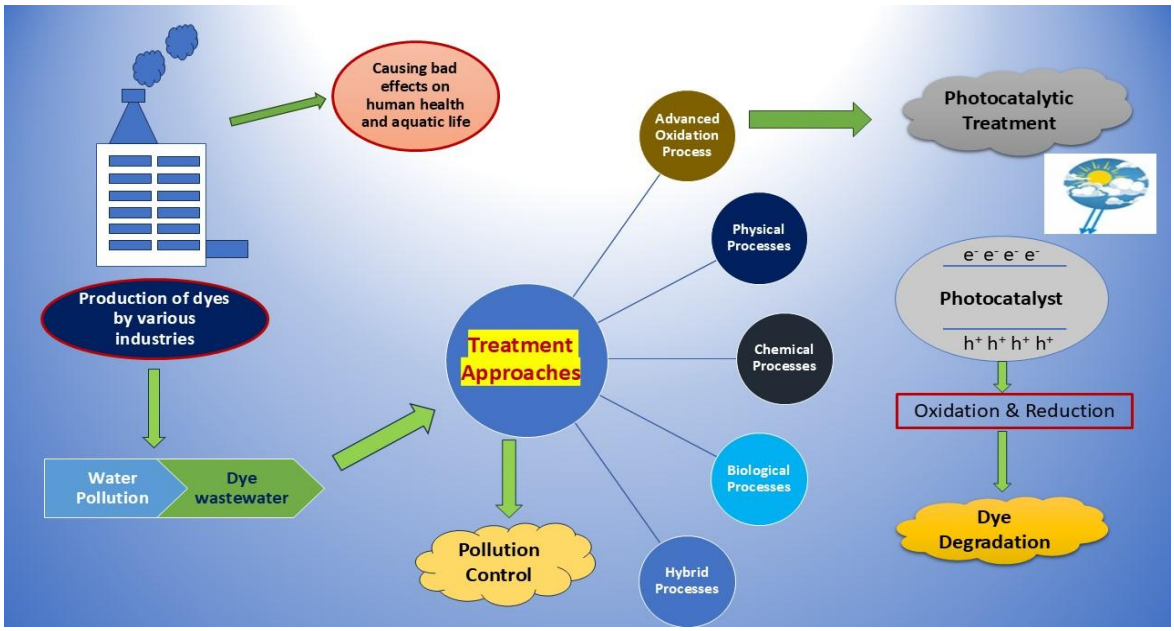

Figure 2: A general view of water pollution by dyes and treatment by various approaches [13].

Nanotechnology in wastewater treatment

Nanotechnology has been established as a promising approach for developing water remediation technologies. Nanomaterials possess unique properties that enable them to effectively get rid of organic compounds and dyes from water. Nanomaterials, such as activated carbons, multi-wall/single-wall carbon nanotubes, metal oxides, and covalent organic frameworks (COFs), are particularly effective in eliminating wastewater pollutants, including heavy metals. Nanotechnology stands as one of the most dynamic fields within material science, offering vast potential for transforming the design, refinement, and properties of various products. Downsizing materials from a macro to a nanoscale brings about significant changes in their optical, magnetic, electrical, antimicrobial, and mechanical characteristics. This transformation is primarily attributed to the increase in surface area and active sites, impacting the physicochemical properties of the materials. Nanomaterials, generally defined as materials with at least one measurement between 1 to 100 nanometers, have revolutionized manysectors, providing sustainable, powerful, and user-friendly products. The remarkable alterations in material characteristics at the nanoscale open up extensive applications in diverse fields such as photocatalytic degradation, storage, and separation. Presently, both institutional researchers and the corporate sector are heavily focused on researching metal oxide (MO) nanostructures, recognizing their significant contributions to sensing, medicine, and renewable energy sources. [17-19] Transition metal oxide nanoparticles display notable surface properties, structural characteristics, and a significant surface area, rendering them appealing options for the adsorption mechanism. [20] The increased chemical activity and a large surface area enable the occurrence of adsorption events. As materials decrease in size from bulk to nano dimensions, their surface-to-volume ratio experiences a significant increase. This reduction in size enhances the surface energy of the adsorbent and introduces active sites for interaction with organic molecules. Consequently, nanomaterials demonstrate superior adsorption capacity compared to bulk materials, particularly in the removal of harmful dyes from wastewater. [21] The use of photocatalysis for removing dye compounds is an effective and promising method for treating wastewater from the textile industry, highlighting the need for developing advanced photocatalysts. This process is environmentally sustainable, as it involves activating a catalyst with light of a specific wavelength to boost reaction rates without the catalyst being consumed. Photocatalysis is widely employed in water treatment systems to decompose harmful pollutants—both organic and inorganic—along with microorganisms, converting them into harmless byproducts like CO2 and water through oxidizing free radicals formed on the catalyst's surface. [22]

TiO_2 nanoparticles for dye degradation

Nanomaterials are commonly employed as photocatalysts for breaking down organic pollutants, such as dyes like methylene blue (MB), EDTA, Rhodamine-B (RB), and Methyl Orange (MO), to help purify water. In the photocatalytic oxidation process, these pollutants are degraded when exposed to semiconductor photocatalysts, light with sufficient energy, and an oxidizing agent like air or oxygen. Semiconductors have a band gap that separates the valence band (VB) from the conduction band (CB). To effectively degrade contaminants, the catalyst must have a suitable band gap and proper band edge potentials. When photons with energy equal to or greater than the band gap are absorbed by the semiconductor, electrons in the valence band are excited and move to the conduction band, generating charge carriers. For the photocatalytic reaction to proceed efficiently, it is crucial to minimize the recombination of these charge carriers (electrons and holes) after they are separated. The semiconductor photocatalytic process is a cost-effective and sustainable treatment technology that aligns with zero work schemes, which is especially desirable for the industry needs. Semiconductor photo-catalysis is one such technology that has shown great potential and fulfills the above requirements. [23] A basic mechanism of photocatalytic dye degradation using TiO_2nanoparticles is given in Figure 3. [24]

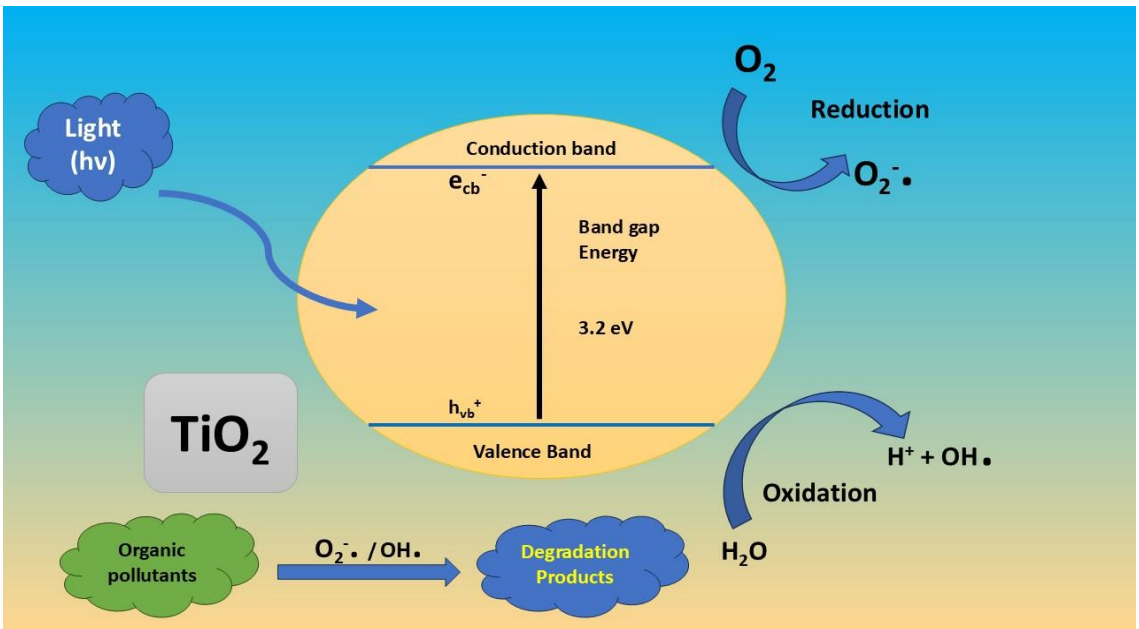

Figure 3: A mechanism for photocatalytic degradation of dyes using TiO_2 nanoparticles [24]

There are many oxidesemiconductors-based photocatalysts available but, titanium dioxide has emerged as the most prevalent choice. This is primarily attributed to its robust oxidizing potential, non-toxic nature, and sustained photostability over extended periods. [25] TiO_2 has found extensive application in photocatalysis owing to its chemical stability and widespread availability in commercial markets. Various types of TiO_2 nanomaterials have been synthesized, such as nanoparticles, nanotubes, nanofibers, and nanosheets. [26] Photocatalysis with TiO_2 nanomaterials as the catalyst stands out as the most promising and advanced destructive technology. The primary benefit of the photocatalytic process lies in its inherently destructive nature, which does not require mass transfer and can be conducted under ambient conditions, with atmospheric oxygen serving as the oxidant. This process has the potential to completely mineralize organic carbon into CO_2. Additionally, nanostructured TiO_2 photocatalysts are widely available, cost-effective, non-toxic, and exhibit high chemical stability. Furthermore, the TiO_2 photocatalytic process is gaining more attention due to its low cost, particularly when sunlight is used as the irradiation source. [27] TiO_2 nanomaterials have been effectively utilized for the photocatalytic treatment of various organic pollutants, including hydrocarbons, chlorinated hydrocarbons, phenols, chlorinated phenols, surfactants, pesticides, and organic dyes. Additionally, they have proven successful in the reductive deposition of heavy metals like Pt^{4+}, Pd^{2+}, Au^{3+}, Rh^{3+}, and Cr^{3+} from aqueous solutions. TiO_2 nanomaterials have also demonstrated efficiency in the destruction of biological materials, including bacteria, viruses, and molds. [28-32]

One significant limitation of TiO_2 nanoparticles is their relatively wide band gap (~3.2 eV), which restricts the efficient absorption of most sunlight. Additionally, the recombination of photogenerated electron-hole pairs occurs rapidly, typically within 10^{-9} to 10^{-12} seconds. To address these issues, extensive research has focused on enhancing the photocatalytic activity of TiO_2, including doping with metal ions can alter the surface properties of TiO_2, slow down the recombination of electron-hole pairs, and increase the number of active sites. [33]

Transition metal doped TiO_2 nanoparticles for dye degradation

The photocatalytic degradation of XRG-dye using Fe^{2+}-TiO2 and Fe^{3+}-TiO2for 1g/litre concentration of nanoparticles shows better degradation efficiencyfor Fe^{3+}-TiO_2after one hour of UV irradiation, the degradation efficiency also improves for visible light can be attributed to band gap tuning by iron doping. Fe^{3+}-TiO_2 exhibited superior photocatalytic activity over Fe^{2+}-TiO_2 in both UV and visible light degradation of XRG. The higher degradation efficiency with Fe^{3+} can be attributed to its greater ability to generate reactive oxygen species (ROS) and promote electron-hole separation, leading to more effective photocatalysis. Under visible light, however, both catalysts showed lower degradation compared to UV irradiation, highlighting the importance of UV light for TiO_2-based photocatalysts. [34, 35]

At a concentration of 0.33 g/L, sol-gel prepared Fe^{3+}–TiO_2 was tested under visible light for the degradation of sulforhodamine-B (SRB), achieving 60.5% degradation in 90 minutes. Fe^{3+}–TiO_2 was effective in degrading SRB under visible light irradiation, though the degradation rate is slower compared to UV-induced degradation of XRG. The effectiveness of Fe^{3+} doped TiO_2 under visible light indicates a potential application for visible-light-driven photocatalysis, though further optimization is required to improve its efficiency. [36]

The sol-gel prepared 0.1 wt. % Fe-TiO_2 exhibits almost complete degradation of X-3B dye solution in a highly acidic medium within one hour. This suggests that Fe doping at a 0.1 wt. % concentration significantly enhances the photocatalytic activity of TiO_2, particularly in UV light, leading to high efficiency in removing organic dyes. For sol-gel prepared nanoparticles, the temperature at which the nanoparticleshave been calcined also determines the activity for photocatalysis. [37]

Fe^{3+}-TiO_2photocatalyst was synthesized using a combined method of sol-gel and hydrothermal techniques.0.15 at. % Fe^{3+}–TiO_2 at 1 g/L under visible light for XRG solution showed remarkable degradation. The higher surface area and better topological properties of these nanoparticlescan be attributed for improved degradation of the dye. The increased surface area facilitates more adsorption of the pollutant and improves the catalyst's overall efficiency. This result highlights the role of surface properties in optimizing photocatalytic degradation under visible light. [38]

Fe–TiO_2 photocatalyst, was used for degradation of methylene blue (MB) solution and gives faster and adequate degradation in acidic solution. The 3 wt. % Fe–TiO_2 catalyst achieved a significant reduction in MB concentration under UV irradiation, although the efficiency was lower than that observed for the X-3B degradation. This suggests that the photocatalytic activity is also dependent on the type of dye, with some compounds being more resistant to photocatalytic degradation than others. [39]

Nitrogen doping has resulted in a significant improvement of the degradation efficiency of Fe^{3+}–TiO_2 for rhodamine B (RB) and resulted in the complete degradation of dye in the visible light region. The nanoparticles were pre-prepared by the combined method of sol-gel and hydrothermal technique. Nitrogen doping likely expands the visible light absorption range of TiO_2, contributing to the high degradation efficiency. This modification shows promise for improving the photocatalytic activity of TiO_2 under visible light, particularly for organic dye removal. [40]

Nanoparticles of$Fe(OH)_3$–TiO_2 and $Cu(OH)_2$–TiO_2 showed significant improvement in the degradation of methyl orange (MO) under UV irradiation, with the half-life of MO reduction dramatically decreased. This indicates that modifying TiO_2 with Fe and Cu hydroxides enhances its photocatalytic activity, likely due to the introduction of additional active sites and improved charge separation, which accelerates the degradation of organic pollutants. [41]

Fe^{3+}–TiO_2 consistently outperformed Fe^{2+}–TiO_2 in UV irradiation tests, but the latter showed slightly better visible light activity in some cases. Visible light degradation generally took longer than UV-induced degradation. Fe^{3+} doping enhanced photocatalytic activity, with higher doping concentrations (0.15 at. %) showing the best results. Doping with nitrogen (Fe^{3+}–TiO_2) also significantly improved performance under visible light. Fe^{3+}–TiO_2 and nitrogen-doped Fe^{3+}–TiO_2 achieved near-complete or complete degradation in several tests (e. g., RB, XRG), while Fe–TiO_2 with higher Fe concentrations (>1 at. %) showed reduced activity, likely due to excessive recombination of electron-hole pairs. Catalysts with higher surface areas and optimized preparation methods (e. g., Fe^{3+}–TiO_2 with 0.15 at. % doping) demonstrated better photocatalytic activity, emphasizing the importance of synthesis conditions in enhancing photocatalytic efficiency.

1% Cu–TiO_2 at 0.5 g/L achieved total degradation (99% mineralization) of 400 mL of 2×10^{-4} M acid orange 7 (AO7) under UV irradiation (254 nm) within two and half hours. The synthesis involved titanium isopropoxide (TIP) and Cu $(NO_3)_2 \cdot 3H_2O$ as base materials forthe sol-gel method. The method used for synthesis (both sol-gel and photo-deposition) and calcination temperature are key factors in achieving good surface area and effective degradation. The results are impressive, with UV irradiation at 254 nm proving highly effective. [42]

Cu^{+} and Cu^{2+}-TiO_2 nanotubes exhibited excellent photocatalytic efficiency for rhodamine B (RB) degradation, achieving 97.5% degradation in a relatively short time (50 minutes). Using an autoclave and ultrasonic treatment likely enhanced the structural properties of the nanotubes, improving surface area and catalysis efficiency. However, the high concentration (5 g/L) of catalyst, might have influenced the high degradation rate. [43]

Titanium-niobium mixed oxide at a concentration of 1.184 g/L achieved complete degradation of 25 mL of 14.24 mg/L brilliant green (BG) dye under UV irradiation within 18 minutes in an extremely acidic solution. This process involved injecting titanoniobate colloids into sulfuric acid. The rapid degradation can be attributed to the synergetic properties of titanium and niobium oxides, which may enhance photocatalytic activity through improved charge separation and light absorption. However, the small volume and high concentration of the pollutant make this result difficult to directly compare with larger-scale applications. [44]

A 1 mol% V-doped TiO_2 at 2.8 g/L achieved 75% degradation of MB under UV–vis irradiation in 4 hours. The nanoparticles were synthesized using the sol-gel method followed by calcination. V-doped TiO_2 exhibited a moderate photocatalytic performance with 75% degradation of MB in 4 hours, vanadium doping can enhance photocatalytic properties through improved charge carrier separation. However, this catalyst showed a lower surface area and efficiency under UV–Vis light compared to the other catalysts. [45]

Zn-doped TiO_2 achieved complete degradation of methyl orange (MO) under UV irradiation in 30 minutes. The synthesis involved titanium-isopropoxide and Zn $(CH_3CO_2)_2.2H_2O$ as precursors, followed by a Stearic acid gel method and calcination, resulting in a surface area of 152 m^2/g. Zn-doped TiO_2 performed excellently in degrading MO under UV light, with complete degradation in just 30 minutes. The use of zinc doping enhances photocatalytic activity by introducing additional active sites for degradation and improving surface area. This catalyst stands out for its high efficiency and relatively short degradation time. [46]

Sr-doped TiO_2 ($SrTiO_3$–TiO_2) at 8 g/L achieved 95% degradation of RamazolBrilliant Blue (RBB) under UV irradiation (325 nm) in 3 hours. These nanoparticles were synthesized by a sol-gel reaction and reversed suspension polymerization, with calcination at 500°C. Sr-doped TiO_2 showed high degradation efficiency (95%) but required a long reaction time (3 hours) compared to the other photocatalysts. The relatively high concentration (8 g/L) of the catalyst is notable, and while it exhibited good photocatalytic activity, its slow degradation rate suggests that the material might be more suited for processes with a longer reaction time or larger-scale applications. [47]

A 3 mol% Bi^{3+}-doped TiO_2 at 1.25 g/L achieved 94.4% degradation of 25 mL of 20 mg/L MO under UV irradiation in 1.5 hours. The synthesis used $TiCl_4$ and Bi $(NO_3)_3 \cdot 5H_2O$ as base materials. Bi^{3+}-doped TiO_2 displayed good photocatalytic performance with 94.4% degradation of MO in 1.5 hours. The use of Bi^{3+} doping is beneficial for enhancing photocatalytic properties, as it may extend the light absorption range and improve electron-hole separation. However, its performance is slightly lower than other catalysts like Zn-doped TiO_2, but still represents a promising material for the degradation of organic pollutants. [48]

Bi/S-doped TiO_2 at 1 g/L achieved 100% degradation of indocyanine (IC) dye, under visible violet light within 40 minutes. The synthesis involved TTB, Bi $(NO_3)_3 \cdot 5H_2O$, and thiourea as base materials, followed by calcination at 400°C for 4 hours. Bi/S-doped TiO_2 is particularly effective under visible light, achieving 100% degradation of IC in just 40 minutes. This result is noteworthy since it highlights the potential for photocatalysts to be activated by visible light, which is more energy-efficient than UV light. The presence of sulfur likely plays a key role in increasing the material's visible light absorption, making this catalyst an excellent choice for sunlight-driven applications. [49]

Cr^{3+}-doped TiO_2 nanomaterials at 0.5 g/L achieved 96.9% degradation of 100 mL of 20 mg/L MO under UV–vis irradiation in 3 hours. The preparation involved using titanium tetrabutoxide and chromium nitrate as base materials, followed by heating at 150°C for 12 hours in a Teflon vessel, and calcination at 300°C for 2 hours. Cr^{3+}-doped TiO_2 showed high degradation efficiency (96.9%) for MO under UV–Vis irradiation, though the reaction took a relatively long time (3 hours). The photocatalytic activity is enhanced by the doping of Cr^{3+}, which improves charge separation and electron transfer. However, the long reaction time indicates that further optimization of this material is needed to reduce the degradation time. [50]

Doping with Cu, Zn, and Bi significantly enhanced photocatalytic activity, especially in UV light, while other metals like V, Sr, and Cr showed moderate performance. The concentration of the catalyst and the pollutant also played an important role in determining degradation efficiency. Higher concentrations of the catalyst (e. g., 8 g/L Sr-doped TiO_2) often led to longer reaction times, though still efficient. Catalystswith higher surface areas (e. g., Zn-doped TiO_2 with 152 m^2/g) generally exhibited higher photocatalytic performance, as this increases the availability of active sites for the photocatalytic reaction.

It is widely recognized that the complete decolorization of organic dyes does not necessarily indicate that the treated water is completely safe. This is because transparent byproductscan be even more toxic, compared to the original dyes. So, achieving the desired water quality requires an equal focus on the mineralization of organic dyes. Wong et al. [42] demonstrated complete color removal and a 99% reduction in total organic carbon (TOC) from acid orange 7 (AO7) within two and half hoursusing 1 at. % Cu–TiO_2. Similarly, in another study, researchers achieved full mineralization of MO within half an hour using 0.1 at. % Zn–TiO_2. [46]

In research by Zhu et al. [38], an optimal Fe^{3+} dopant concentration of 0.15 at. % was found for Fe^{3+}-modified TiO_2. The doping of Fe^{3+} significantly enhanced the formation of oxygen vacancies within the TiO_2 lattice and on its surface, improving water adsorption, hydroxyl group formation, and photocatalysis. Fe^{3+} doping plays a major role in the effective separation of electrons and holes that were excited by light. However, for the increased concentration of Fe^{3+} dopant, the rate of recombination increases, competing with the redox processes. This was observed in Qi et al. 's study [37], where the optimal dopant concentration was found to be 0.1 wt. %. Excessive iron deposition on TiO_2 led to the formation of Fe $(OH)_2^+$, which reduced the light energy reaching the TiO_2 surface, as Fe $(OH)_2^+$ absorbed light in the 290–400 nm range and decreased degradation of X-3B.

TiO_2 nanoparticles with 1% Cu doping have the highest efficiency in both decolorizing and mineralizingAO7 [41]. However, increased copper concentration resulted in reduced photo-degradation activity due to increased electron-hole recombination, and excessive Cu could also hinder the absorption of incoming photons by TiO_2. The 0.1 at. % Zn–TiO_2 nanocatalysts were the most effective in photodegrading MO [46], with the optimal dopant concentration reflecting a delicate balance between an increase in trap sites (which enhances efficient trapping) and a reduction in trapped carriers (leading to longer charge transfer lifetimes at the interface).

The photocatalytic activity of Sr-doped TiO_2 microspheres significantly decreased as the dipping time during preparation increased [47]. An excess of $SrTiO_3$ covered nearly the entire surface of the microspheres, reducing synergistic effects and limiting the photo-degradation efficiency of anatase TiO_2. Another study observed that Bi^{3+} doping in TiO_2 improved the photo-degradation of methyl orange up to a concentration of 3%, beyond which activity declined. The improved photocatalytic performance of Bi^{3+}-doped TiO_2 was linked to the formation of the $Bi_4Ti_3O_{12}$ phase. However, when the bismuth doping exceeded 3%, excess bismuth ions aggregated into Bi^{3+} clusters, which acted as a trap center for charge carriers and reduced photocatalytic degradation efficiency. [48]

Regarding modification strategies, heavy metals are typically used to modify TiO_2 through doping, although solid evidence for this is often lacking. Convincing pieces of evidence are there that Fe exists in a trivalent ionic state, substituting Ti^{4+} in the TiO_2 lattice. [38] This was confirmed through various characterization techniques. The replacement of Fe^{3+} for Ti^{4+} likely results in the formation of a negatively charged mineral capable of binding cations and degrading organic compounds.

Few studies have used visible light for photocatalysis. One used a 150W Xe lamp to degrade sulforhodamine B (SRB) with iron-doped TiO_2, which showed a red shift in its band-gap transition to 435 nm compared to pure TiO_2 (360 nm). [36]One study used visible light (>380 nm) to degrade acid yellow XRG dye with Fe3+-doped TiO_2, finding enhanced photocatalytic activity in 0.15 wt. % Fe^{3+} TiO_2 [38]. Cong et al. [40] employed a 1000W halogen lamp (>420 nm) to degrade RB solution with nitrogen-and Fe^{3+}-codoped TiO_2, achieving full degradation in 4 hours. This was attributed to band-gap narrowing and multiple excitation pathways, improving solar energy utilization. However, visible light degradation generally takes longer than UV light. [38] In an exceptional case, full and quick degradation of indigo carmine (IC) solution was achieved under visible violet light using Bi-and S-codopedTiO_2. [49] This underscores the potential for developing innovative modified TiO_2 photo-catalysts with increased performance under visible light, marking it as a potential field for future research.

2. Conclusion

Titanium dioxide is widely used for treating organic compounds in wastewater, prompting significant efforts to modify this semiconductor material in recent years. This review highlights various TiO_2 photocatalytic modifications aimed at improving efficiency, visible light activity, and catalyst reuse, focusing on the use of transition metals like Fe, Cu, Zn, Sr, and Cr. While these modifications have shown success in enhancing TiO_2's effectiveness in laboratory-scale wastewater treatment, there is still a need to develop pilot-scale systems and apply the technology to cost-effective dyehouse effluent purification. Transition metal-doped TiO_2 nanoparticles offer promising advances in wastewater treatment, particularly under visible light, but challenges related to stability, environmental safety, and optimal doping strategies need to be addressed. Continued research is essential to overcome these obstacles and improve the practical use of photocatalytic materials in environmental remediation, offering significant ecological and economic benefits to the commercial sector.

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