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Mini Review

An Overview on the Photocatalytic Degradation of Organic Pollutants using TiO_2 and Metal doped TiO_2 from Industrial Wastewater

Ashish Kumar and Shivalini Singh*

Department of Chemistry, Agra College, Agra 282001, **INDIA**
Email: shivalini.chaharag@gmail.com

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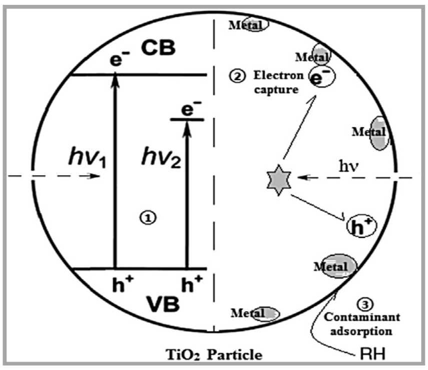
ABSTRACT

Organic compounds, which are produced by various industries, result in a variety of contaminant problems. TiO_2 based photocatalysts can be used to improve the quality and quantity of organic molecules in wastewater. TiO_2 is better because of its nontoxicity, strong degradation ability, and great thermal and chemical stability. The annihilation or transformation of dangerous chemical wastes to harmless end-products, such as CO_2 and H_2O, is the purpose of titanium dioxide nanoparticles, which are meant to be both supplemental and complimentary to current water-treatment technologies. The use of doped TiO_2 nanoparticles in photocatalytic waste water degradation has shown enormous potential in eliminating these complex organic pollutants. Visible light and solar light may now be used effectively as a light source because to advancements in the properties of doped TiO_2 nanoparticles. Doped TiO_2 nanoparticles have a lot of potential in terms of water and energy issues because they have two main characteristics: they are effective at eliminating pollutants that are persistent in nature and they use energy efficiently. The relevance of doped TiO_2 nanoparticles in the water-energy nexus is briefly discussed in this context. As a result, this paper examines and summarises recent efforts in the field of titania nanoparticle synthesis, modifications, and water treatment applications.



Mechanisms of metal-doped TiO_2 photocatalysis.

Keywords: TiO_2 photocatalyst, Metal doped TiO_2, Photocatalytic degradation, Organic pollutants, Wastewater.

INTRODUCTION

The contamination of wastewater with toxic organic solvents is one of the main environmental concerns. The presence of organic pollutants in water supplies causes vital harm to human health as well as aquatic organisms and restricts exposures to sunlight for aquatic plant and animal species, thus altering the aquatic environment [1].

Industrial progress is intimately related to toxic chemicals that are damaging to individuals, the environment, and hard to break down naturally, such as dyes and phenolic compounds, which are typically found in industrial effluents [2]. Large quantities of organic effluents are being discharged from textile, leather, paint, and other industries into water bodies [3, 4].

Industrial discharges are complex combinations of chemical and biological compositions that have multiple environmental impacts depending on the source of the toxicant [5]. Because of the carcinogenic and mutagenic effects, organic pollutants are of significant consequences even after exposure to small concentrations types of pollutants [6].

The rapid rise in the use of organic pollutants in manufacturing poses a risk to the protection of the environment and human health [7]. It is inevitable to manage wastewater before disposal into the atmosphere to preserve human life and environmental sustainability [8].

Many novel methods have recently been developed for the degradation of organic pollutants in order to reduce their harmful effects on the environment. These organic contaminants in industrial wastewater are removed using a number of techniques, including biological [9, 10], chemical, physical [11] and advanced oxidation processes (AOPs) [12, 13]. For the degradation of industrial effluents, photocatalysis is also one of the most effective and commonly utilised techniques. A heterogeneous catalyst has been excited in photocatalytic degradation processes using a variety of light sources. Using sunlight rather than UV radiation makes photodegradation procedures more cost-effective [14, 15]. Organic pollution remediation frequently employs the photocatalytic agent titanium dioxide. [16]. Pure TiO_2 has a significant bandgap, which makes it more susceptible to excitation when exposed to UV radiation, and a high rate of electron-hole (e+/h-) pair recombination, which results in a relatively low photocatalytic efficiency. But a model photocatalyst needs to have a bandgap that allows for visible light stimulation [17]. As a result, substituting oxygen in the TiO_2 lattice to reduce the optical energy bandgap is one way to adjust inner band structure of TiO_2 and cause visible light absorption. [18]. TiO_2 can absorb more visible light or be more reactive in the UV range by being doped with metal ions [19]. By reducing the capacity for photocatalysis in conjunction with thermal instability, metallic components can generate a sufficient bandgap shift and encourage recombination. [20]. Metal doped TiO_2 nanophotocatalyst and the photocatalytic degradation of organic contaminants in wastewater generated through diverse industrial processes is the main topic of the current review.

Photocatalysis: Solar power is a renewable resource and effective use of solar power is one of the key priorities of modern science and engineering to control environmental emission through the use of photocatalysis [21].

Photocatalysts are widely used to purify wastewater, since they help to increase catalyst reactivity by possessing a higher surface ratio and shape dependent characteristic [22].

Photocatalysis is a degradation of the substances in the presence of light energy [23]. As light strikes the catalyst during photocatalysis, it absorbs sufficient energy to become activated by light equal to its energy bandgap. In a photocatalytic system, photogenerated species like e^-/h^+ pairs are formed on the surfaces of photo-excited nanoparticle catalysts, which react with oxygen molecules or hydroxyl groups to produce reactive oxygen species. These species then go for the organic molecules in the wastewater and oxidise them to break them down. As a result, e^-/h^+ couples are created on the catalytic surfaces of photoexcited nanoparticles. [24]

Nanophotocatalyst have been shown to be able to increase the oxidation potential due to the efficient production of oxidising species on the surface of the material, which effectively leads to the degradation of toxicants from wastewater [25]. Indeed, combining a semiconductor with sunlight to eradicate pollutants [26] could provide a sustainable solution to critical environmental pollution problems [27].

The ability of a photocatalytic reaction to degrade organic pollutants arises from the redox environment generated from the photoactivation of a semiconductor such as titanium dioxide (TiO_2). Because it can break down a variety of organic contaminants, TiO_2 is one of the most used photocatalysts. Since then, water and wastewater treatment have received a lot of attention as titania photo electrolysis applications. [28].

Mechanism of Titanium dioxide (TiO_2) photocatalysis: For the past two decades, photocatalytic degradation of diverse organic and inorganic contaminants employing semiconductor oxide as a photocatalyst has been widely used in wastewater. Many semiconductor oxides exhibit good photocatalytic activity. [28]. Among these, nanosized TiO_2 is one of the most promising and has extensively researched as a photocatalyst in wastewater treatment among a large number of photocatalyst because of its high photoreactivity, low cost, nontoxicity and prolonged corrosion stability [29].

Moreover, TiO_2 exist in three natural states, anatase, rutile, and brookite [30]. TiO_2 nanoparticles can photodegrade many organic molecules when exposed to UV or visible light, including alcohols [31] and phenols [32], colourants [33] and Carboxylic acids [34]. As the most promising semiconductor photocatalyst, TiO_2 based materials are also expected to play a vital role in addressing serious environmental and pollution concerns as well as reducing the energy crisis. [35].

TiO_2-mediated semiconductor photocatalysis has attracted a lot of attention because of its capability in overall destruction of organic pollutants via photocatalytic oxidation. A general mechanism is illustrated in figure 1 [36].

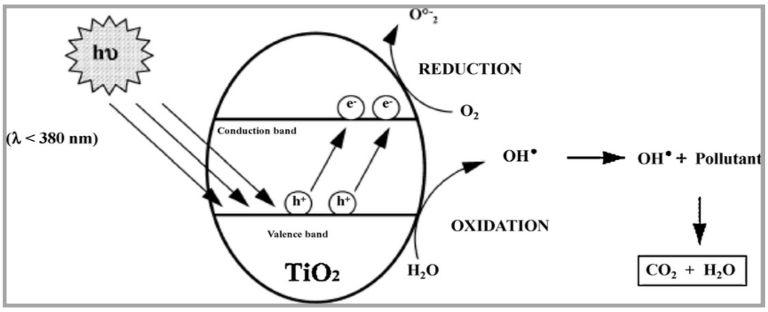


Figure 1. General mechanism of the TiO_2 photocatalysis [36].

Excitation of TiO_2 under photon irradiation with energy greater than the TiO_2 band-gap energy initiates the photocatalytic oxidation process. Photogenerated electron (e^-) and hole (h^+) pairs will travel to the surfaces of superoxide radical anion (O_2) and hydroxyl radical anion (OH) without recombination. These reactive oxygen species are primarily responsible for the oxidation of organic compounds in water. [37].

The following concise description can be used to sum up photogeneration of radical species in the TiO_2/UV system [38].

$$TiO_2 + h\nu\ (UV) \rightarrow TiO_2\ (e_{CB}^{-} + h_{VB}^{+}) \qquad \ldots (1)$$

$$TiO_2\ (h_{VB}^{+})\ OH^{-} \rightarrow TiO_2 + OH^{\bullet} \qquad \ldots (2)$$

$$TiO_2\ (h_{VB}^{+})\ OH^{-} \rightarrow TiO_2 + OH^{\bullet} \qquad \ldots (3)$$

$$TiO_2\ (e_{CB}^{-}) + O_2 \rightarrow TiO_2 + O^{-\bullet} \qquad \ldots (4)$$

$$O_2^{-\bullet} + H + HO_2^{\bullet} \qquad \ldots (5)$$

$$Dye + OH^{\bullet} \rightarrow \text{degradation products} \qquad \ldots (6)$$

$$Dye + h_{VB}^{+} \rightarrow \text{oxidation products} \qquad \ldots (7)$$

$$Dye\ e_{CB}^{-} \rightarrow \text{reduction products} \qquad \ldots (8)$$

There are a variety of ways for synthesizing TiO_2 nanoparticles, including sol-gel, sol, hydrothermal, solvothermal, chemical vapour deposition, and so on. [39].

Limitations of TiO_2 based photocatalysis: TiO_2 is regarded as a promising photocatalyst due to its non-toxicity, low cost, and ability to degrade a variety of contaminants. Nevertheless, the photoactivity of this semiconductor can only be induced by UV light stimulation. Due to large band gap of TiO_2 (~3.2eV) and high rate of charge recombination [40] of photogenerated electron/hole (e^-/h^+), usage as a photocatalyst is typically restricted. This lowers the efficiency of photon-to-charge carrier conversion and restricts the use of visible or solar light in photochemical applications. Because of this, only around 3-5% of the sun's incoming energy can be used on Earth's surface, making wastewater treatment applications impractical [41]. In this context, a number of methods have been developed to boost the effectiveness of the photocatalytic process in TiO_2. [42] Several modifications to TiO_2 have been proposed to boost photocatalytic activity of TiO_2: metal doped TiO_2, non-metal doped TiO_2, TiO_2 composites with reduced band gap energy semiconductor [43]. For increased photocatalytic activity on the breakdown of different organic molecules when exposed to visible light, doped TiO_2 with metals such as Cu, Co, Ni, Au, Ag, Pt, etc. has been extensively explored in recent decades.

Mechanism of Metal doped TiO_2 photocatalyst: Metal ion doping appears to be one of the best techniques for improving a catalyst's solar photoactivity because of its synergistic effects on TiO_2 absorption expansion in the visible light field and electron hole pair separation efficiency. [45]. In fact, by trapping electrons and allowing holes to be transported to the TiO_2 surface, the interaction with metal is designed to prevent electron-hole pairs from recombination. [46]. General mechanism of metal doped TiO_2 is shown in figure 2 [47].

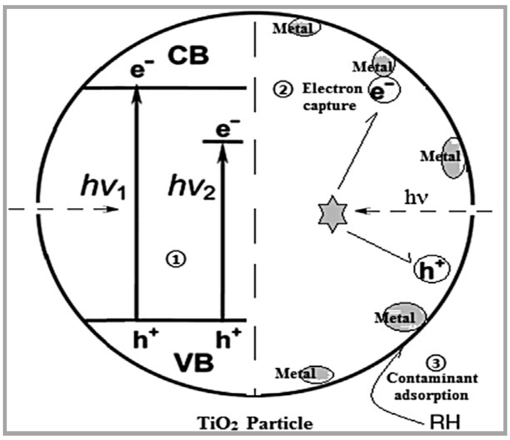


Figure 2. Mechanisms of metal-doped TiO_2 photocatalysis [47].

The energy produced by the metal ion dopant is either at the top of the valence band or creates mid span states during metal-ion doping. As the atomic number of the dopants increases, the localized level decreases in energy, resulting in the generation of the valence band with the electrons O p and Ti 3d. Due to the inclusion of electron states into the TiO_2 band gap, the band gap decreases, resulting in the formation of a new lowest unoccupied molecular orbital gap. [**48**].

Photocatalytic degradation of organic pollutants: In recent years, photodegradation has become one of the most effective methods for reducing organic pollutants in wastewater [**49**]. The efficient breakdown of all types of petrochemical pollutants in water can be accomplished by photocatalytic methods. For a decrease in power usage, using alternate light sources. For the photocatalysis process, it is necessary to create more effective methods for using sun energy [**50**].

Numerous working factors that control the photodegradation of the organic molecule have a significant impact on the oxidation rates and effectiveness of the photocatalytic system. The significance of various viable parameters has been the subject of numerous studies. Photocatalysis is influenced by a number of variables, including dye concentration, catalyst amount, pH, photocatalyst size and structure, surface area, reaction temperature, concentration and nature of pollutants, light intensity and irradiation time, and dopants' effects on dye degradation. It is a promising method because it not only degrades the pollutants but also completely mineralizes them to carbon dioxide (CO_2), water (H_2O), and mineral acids [**51–53**].

When exposed to UV radiation, the semiconductor TiO_2 mineralizes a variety of chemical contaminants, including herbicides, dyes, pesticides, phenolic compounds, tetracycline, sulfamethazine, and others. TiO_2 has a significant band gap (~3.2eV) [**28**].

The presence of two or more oxidation states, often differing by one, is a property of transition metals [**54**]. Due to this property, TiO_2 doped with transition metals increases photocatalytic activity by shifting the optical bandgap from UV to visible light. Transition metals like cobalt (Co), copper (Cu), vanadium (V), tungsten (W), and iron (Fe) have been doped into TiO_2 to enable photocatalytic degradation of organic contaminants under visible light [**55–59**]. Doping TiO_2 with transition metals narrows the band-gap and causes a batho-chromic shift of the absorption edge to the visible-light region, caused by a charge-transfer transition between d electrons and CB or VB [**57**].

Sood S. *et al* [**60**] were synthesized the Fe-doped TiO_2 nanoparticles by a novel and facile ultrasonic assisted hydrothermal method and characterized in detail by various analytical techniques in terms of their morphological, structural, compositional, thermal, optical, pore size distribution, etc properties. The photocatalytic activities of the as-prepared Fe-doped TiO_2 nanoparticles were examined under visible light illumination using para-nitrophenol as target pollutant. By detailed experimental findings revealed that the Fe dopant content crucially determines the catalytic activity of TiO_2 nanoparticles. Suwarnkar M. B. *et al* [**61**] was prepared pure anatase TiO_2 photocatalyst with different Ag contents via a controlled and energy efficient microwave assisted method. The research work is mainly focused on the enhancement of degradation efficiency of methyl orange (MO) by doping of Ag in TiO_2 matrix using UV light (365 nm). A 99.5% photodegradation efficiency of methyl orange was achieved by utilizing 0.25 mol% Ag doped TiO_2 (1 g/dm^3) at pH=3 within 70 min. Machut C. *et al* [**62**] was developed gold-doped titanium dioxide materials with the aid of commercially available and common cyclodextrin derivatives, acting both as reducing and stabilizing agents. Anatase titanium oxide was synthesized from titanium chloride by microwave heating without calcination. Lin C. J. *et al* [**63**] was directly doped TiO_2 with copper sulfate by a sol-gel method to promote its visible light activity (VLA) following a post-calcination step and has been well examined the homogeneous photocatalytic degradation of 2-chlorophenol (2-CP) in titanium dioxide suspensions containing copper ions or/ and sulfates.

CONCLUSION

The health risks associated with the presence of contaminants in water, as a result of typical water treatment systems' incapacity to effectively eradicate organic pollutants, were outlined in the literature under study. TiO_2 nanoparticles have been demonstrated to be capable of completely decomposing organic contaminants in an aqueous media, resulting in the creation of harmless compounds, and so offer enormous potential for use in water treatment processes. However, due to several significant practical problems, its application is restricted. Metal-doped TiO_2 method for enhancement of visible light photocatalytic activity of TiO_2 is one of the recently proposed remedies for increasing the effectiveness of TiO_2-based photocatalytic degradation of organic pollutants. To address these drawbacks and broaden the use of TiO_2-based particles for photocatalytic degradation, more research and development is needed in this field.

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