



REVIEW

Photocatalytic Degradation of Organic, Inorganic and Microbial Pollutants Present in Water by Novel Materials: A Critical Review and Present Update

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Presently water pollution is the one of the major threats faced by living things all over the world. The main cause of water pollution is its effect on the life of aquatic animals. Organic, inorganic, microbial and other pollutants often mix with water bodies mainly due to human activities. Because of the presence of pollutants in water, the amount of dissolved oxygen level can be decreased which in turn affect the survival of aquatic life. The pollutant water may enter the agriculture fields and damage the plants extensively. The methods, such as, coagulation, adsorption, foam floating, electro dialysis, capacitive deionization, etc. are presently employed to treat the waste water. Among these methods, heterogeneous photocatalytic degradation is considered to be a good method because of its low cost and environmental friendliness. In this review, the decontamination of different kinds of organic, inorganic and microbial contaminants in water with different photocatalysts process is presented.

Keywords: Water pollution, Different pollutants, Photocatalytic degradation, Purification of water.

INTRODUCTION

One of the greatest challenges of 21st century is the environmental pollution. Water pollution is the one of the main concern among them. In these days, industries are booming along with human civilization, which leads to many environmental issues and also rises to the point that man cannot control it. Various contaminants specifically chemicals such as organic, inorganic and radiological along-with other impurities such as pathogens are present in water bodies. Now-a-days, there are many different kinds of methods in wastewater treatment for the elimination of the contaminants from water. Semiconductor heterogeneous photocatalysis has a huge potential to treat contaminants in water due to its efficiency to degrade intransigent compounds [1]. Heterogeneous photocatalysis involves photo-induced chemical reactions on the surface of the semiconductor material upon exposure to photons [2]. A photocatalyst is a substance, which is activated by adsorbing a photon and is

able to accelerate a reaction without being consumed [3]. Semiconductor heterogeneous photocatalysis is a versatile, low cost and environment friendly method, which leads to the application for the treatment of low level concentration of pollutants in water [4]. Several studies have been reported till date in treating wastewater by semiconductor based photocatalysis [5].

Photocatalysis has been proven to be the productive and inexpensive tool for the removal of pollutants from water. In photocatalytic degradation process, different types of nanoscale photocatalysts are used. The photocatalytic degradation of 4-chlorobenzoic acid takes place under sol-gel derived TiO₂ films utilizing a quartz batch reactor [6]. Due to high surface area to volume ratio, the nanoscale photocatalysts have attracted much attention. ZnO nanoparticles serve as the good catalysts in photocatalytic degradation of organic contamination by using the fluorescence emission characteristics of ZnO nanoparticles in aqueous solution [7]. Apart from this many inorganic materials, such as ZnS [8], CdS [9], SrO₂ [10], CaO [11], WO₃

[12] and Fe-TiO₂ [13] are used as effective photocatalytic materials to treat wastewater. In this review, we report a broad description about various photocatalysts used to remove the unwanted ingredients such as, organic, inorganic and microbial constituents present in water. The details regarding their impact of various other parameters in the survival of aquatic animals are also presented in this article.

Organic pollutants

Pesticides: Pesticides are the substances which are used to control pests [14]. Unfortunately, the improper handling and application procedure of pesticides lead to many harmful effects on living organisms such as affecting nervous system, liver, reproductive problems and even cause cancers [15]. It was found that all varieties of pesticides directly affect the human health and they render high level toxicity. Photocatalytic degradation is an effective method for the treatment of contaminated wastewater especially pesticide contaminated water [16]. Ahmed *et al.* [17] summarized that certain parameters that depend on the photocatalytic degradation of organic compounds (*e.g.* pesticides and phenol), which include the types and composition of the photocatalyst and light intensity, amount of catalyst, initial concentration of the substances, pH of the reaction medium, type of solvents, ionic components in water, oxidizing agents, catalyst application mode and calcination temperature in the water environment. Affam & Chaudhuri [18] carried out an effective photocatalytic degradation of pesticides *e.g.* chlorpyrifos, cypermethrin and chlorothalonil by the addition of H₂O₂ along with UV/TiO₂ in aqueous solution, while Lhomme *et al.* [19] observed the photocatalytic degradation of chlortoluron and cyprocanazole pesticides in pure water and a commercial agricultural solutions on TiO₂ coated media. Tamimi *et al.* [20] studied the degradation of pesticide methomyl in aqueous solution by UV-irradiation in the presence of TiO₂ Degussa P-25. They found that mineralization to carbon dioxide, water, sulfate and ammonia took place during the process. Liu *et al.* [21] investigated the photocatalytic degradation of profenofos and triazophos residues in Chinese cabbage, *Brassica chinensis*, using a cerium-doped nano-semiconductor TiO₂ (TiO₂/Ce) under the field conditions. They have found that the degradation efficiency of these organophosphate pesticides in *B. chinensis* was significantly enhanced in the presence of TiO₂/Ce. Phytotoxicity symptoms of *B. chinensis* caused by the application of profenofos/triazophos with TiO₂/Ce treatment. Abdennouri *et al.* [22] synthesized TiO₂ and titanium intercalated purified clays and investigated their photocatalytic activity for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichloro-phenoxypropionic acid (2,4-DP) in aqueous solution. Alkayal & Hussein [23] found that removal efficiency increases with the Ti content in the pillared clay. It was found that 2 wt.% of Ag@Mg₄Ta₂O₉ display the best photocatalyst efficiency for atrazine degradation. When the pesticide contaminated water is treated, the influencing factors, such as concentration of pesticide, type and composition of photocatalyst, photocatalyst dosage, wavelength of light, photocatalytic duration and other factors need to be considered for the effective treatment purpose.

Herbicides: Herbicides are the kind of pesticides used to destroy weeds in crops [24]. According to He *et al.* [25], herbicides are the one of the most used chemical substances. When these chemicals are used in an unfair manner, they affect badly on the untargeted organism [26], which leads to many harmful effect on plants [27] as well as animals [28]. Pelizzetti *et al.* [29] carried out the photocatalytic degradation of atrazine and *s*-triazine herbicides by using TiO₂ as photocatalytic under stimulated solar light. The contaminant (atrazine) decomposed in very short time to less than 0.1 ppb. Shifu & Yunzhang [30] studied the photocatalytic degradation of glyphosate by TiO₂ photocatalyst in aqueous dispersion under irradiation by UV light. ZnO is an effective photocatalyst for the decontamination of water in presence of sunlight. Shibin *et al.* [31] carried out solar photocatalytic degradation of pollutant herbicide diquat in water by using ZnO catalyst by following pseudo-first order kinetics. In the field of agricultural water decontamination, sulfonylurea herbicides undergone photocatalytic degradation with TiO₂ catalyst produced a final product of cyanuric acid [32]. Lee *et al.* [33] studied the photocatalytic degradation of picloram in water using titanium dioxide alumina beads (TDABs) with and without UV light source. The picloram degradation rate with UV and TDABs are greater than without UV. Infante *et al.* [34] observed the increased degradation rate of paraquat herbicides by the addition of TiO₂ along with the photolysis in the presence of dissolved oxygen. Abdennouri *et al.* [35] studied the photocatalytic activity of Pt/TiO₂ against two chlorophenoxy herbicides: 2,4-dichloro-phenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) organic pollutants in water. They found that the photocatalytic activity increases with the enhancement of platinum yield in the catalyst. Daneshvar *et al.* [36] studied the photocatalytic degradation of a herbicide, erioglaucine, in water in the presence of TiO₂ nanoparticles (Degussa P-25) under ultraviolet light illumination. Their results showed that the UV/TiO₂ process with Degussa P-25 as photocatalyst was appropriate as the effective treatment method for removal of erioglaucine from a real wastewater. Pelentridou *et al.* [37] studied photocatalytic degradation of a water soluble sulfonylurea herbicide: azimsulfuron in the presence of titania nanocrystalline films. They found that acidic or alkaline media were unfavourable for azimsulfuron photodegradation.

Fungicides: Fungicides are the biological chemical compounds used to inhibit the growth of fungi in crops. Improper and overdosage of fungicides cause many health issues, especially when contaminated in water. Danion *et al.* [38] have carried out the photocatalytic degradation of imidazolinone fungicide, fenamidone in a TiO₂ coated optical fiber reactor with first order kinetic and 0.02 h⁻¹ degradation rate constant, which results in the formation of sulfate ions and carboxylic acid. The sulfates have partial adsorption onto TiO₂. Saïen & Khezrianjoo [39] made an attempt to investigate the photocatalytic degradation of carbendazin fungicides by only UV-irradiation and UV/TiO₂, in which UV/TiO₂ provides much better results. Accordingly, more than 90% of the fungicides degraded in moderate and suitable conditions with catalyst concentration (70 mg/L), natural pH (6.73), ambient temot (25 °C) and 75 min irradiation time.

The photocatalytic degradation of the fungicide fenhexamid also carried out by TiO₂ suspension under stimulated solar light [40]. The presence of alcohols have some effects on the degradation of pesticides. Hazime *et al.* [41] observed the influence of alcohol on the degradation of imazalil along with the photocatalytic degradation in an aqueous suspension of TiO₂. The presence of alcohol in the solution inhibits the degradation of imazalil. From these reviews, it is clear that polymer composite TiO₂ based photocatalyst is more efficient than the neat TiO₂. Thakare & Bhave [42] carried out the photocatalytic degradation of thiram pesticide on TiO₂-PVA polymer composite photocatalyst under visible light leads to a complete degradation of thiram pesticide by 150 min with the end products of CO₂, nitrate and sulphate. Similarly, the photocatalytic degradation of a triazole pesticide-cyproconazole in water by UV/TiO₂ photocatalyst using industrial TiO₂ coated non-woven paper was reported by Lhomme *et al.* [43].

Insecticides: Insecticides are the substances used to kill insects in agriculture. As like other pesticides, photocatalytic degradation is an effective method for the degradation of insecticide contaminants in water. Harada *et al.* [44] have studied the photocatalytic degradation of organophosphorous insecticides, dimethyl-2,2-dichlorovinyl phosphate (DDVP) and dimethyl-2,2,2-trichlorohydroxyethylphosphonate (DEP) in presence of suspended TiO₂ illumination with super high pressure mercury lamp or by exposure to sunlight. The platinum loading to H₂O₂ enhanced the degradation rate, which found to be 4.5- and 6-fold for DDVP and DEP, respectively. The degradation products were Cl⁻, PO₄³⁻, H⁺ and CO₂ along with the formation of an intermediate formaldehyde. Researchers [20,45] have observed that photocatalysis is an excellent new advanced oxidation technology (AOT) to eliminate methomyl present in water. The carbamate insecticide methomyl can also be removed from the contaminated water by photocatalytic degradation on TiO₂ Degussa P-25 photocatalyst by UV irradiation. The complete disappearance of 1.23×10^{-4} mol⁻¹ of pure pesticide takes place with 45 min of illumination and 80% of total organic carbon removal takes place in less than 4 h. Lee *et al.* [46] have prepared sulfate-doped silver phosphate (SO₄-Ag₃PO₄) using a simple precipitation method and they evaluated its visible light photocatalytic activity against seven neonicotinoid insecticides currently available on the market. The degradation followed the order of thiacloprid > nitenpyram > imidacloprid > clothianidin > acetamiprid > thiamethoxam > dinotefuran. Mir *et al.* [47] have studied the photocatalyzed degradation of an insecticide, thiamethoxam in aqueous suspension of TiO₂. They have found that low H₂O₂ dosage enhances degradation whereas overdose retards it. They have concluded that the toxicity of thiamethoxam decreases with the increase in irradiation time. Grover *et al.* [48] have demonstrated the influence of Ag-loading (0.2-1.0 wt %) onto sodium titanate nanotubes (TNT) for complete photomineralization of the neurotoxic imidacloprid insecticide under UV light illumination. They have reported that degradation of IMI follows pseudo-first-order kinetics. Tomašević *et al.* [49] have studied the photocatalytic degradation of carbamate insecticide carbofuran in water using polychromatic light and ZnO and

TiO₂ catalysts. They have reported that almost complete removal of 88.4 mg L⁻¹ of carbo-furan occurred within 2 h under optimized conditions.

Nematicides: A nematicide is a type of pesticide used to kill plant parasitic nematodes. Carbofuran has toxic effect on human include biochemical hematological & immunological effects and some serious effects on the maternal-placental-fetal-unit [50]. It was reported the pesticide emigrates from treated field to air, other land and water bodies. So, it is required to treat the contaminated water [51]. Katsumata *et al.* [52] have reported that the photocatalytic degradation is an effective technology for the treatment and mineralization of carbofuran contaminated water. They have reported that the decrease of TOC content was observed during the photocatalytic process and the removal percentage obtained was about 70% after 25 h. Fenoll *et al.* [53] studied the solar-photocatalytic degradation of carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl-carbamate) in leaching water using ZnO and different mixed phase (rutile/anatase) TiO₂ at pilot plant scale. They have found that the primary degradation of carbofuran followed pseudo-first order kinetics. Mahalakshmi *et al.* [54] also studied the photocatalytic degradation of carbofuran in an aqueous solution using Degussa P-25 TiO₂ and ZnO as photocatalysts. The effects of various experimental parameters such as initial concentration of carbofuran, pH of the solution, catalyst loading and light intensity were systematically studied in order to achieve maximum degradation efficiency. Finally, they have reported that the degradation with ZnO showed less efficiency than TiO₂.

Dyes: The wastewater containing dye effluents is highly toxic to microorganisms, aquatic life and human [55]. The photocatalytic degradation is an effective method for the complete degradation of dye and hence it may be a viable technique for the safe disposal of textile wastewater into water streams [56]. Natarajan *et al.* [57] have found that higher surface area of photocatalysts plays a major role in photocatalytic degradation of dyes, which leads to the higher adsorption of dye molecule on the surface of photocatalyst and enhances the photocatalytic activity. Han *et al.* [58] have explained about heterogeneous photocatalysis involving TiO₂ in removing the toxicity of the dyes and their visibility in surface water. Houas *et al.* [59] studied the TiO₂/UV photocatalytic degradation of methylene blue in aqueous heterogeneous suspensions. They have found that TiO₂/UV-based photocatalysis could simultaneously oxidize the dye with almost complete mineralization of carbon and of nitrogen and sulfur heteroatoms into CO₂, NH₄⁺, NO₃⁻ and SO₄²⁻, respectively. Rauf & Ashraf [60] have reviewed the advanced oxidation processes (AOPs) for application in degradation studies. They have summarized and highlighted the effect of a variety of conditions on TiO₂-photocatalyzed decoloration of dyes, such as, amount of catalyst, reaction pH, light intensity, concentration of organic dye and the presence of ionic additives. Yuan *et al.* [61] have studied the photocatalytic degradation of methylene blue in aqueous solution using TiO₂ immobilized on activated carbon fibers. They have found that the TiO₂/ACF composite could be used repeatedly without a decline in photodegradation ability. Mohamed *et al.* [62] developed highly efficient photocatalyst

based on composite nanofibers containing polyacrylonitrile (PAN), carbon nanotubes (CNT) and surface functionalized TiO₂ for the degradation of model molecules, methylene blue and indigo carmine, under UV irradiation in aqueous solutions. Further, they have investigated the effective factors on the degradation of the dyes, such as, the amount of catalyst, solution pH and irradiation time. Kuriakose *et al.* [63] studied the sunlight driven photocatalytic degradation of methylene blue and methyl orange dyes in water to evaluate the photocatalytic activities of Cu doped ZnO nanostructures using UV-visible absorption spectroscopy. They have reported that the enhanced photocatalytic activity of Cu-ZnO nanostructures is attributed to the combined effects of improved separation of photo-generated charge carriers due to optimal Cu doping in ZnO nanostructures and the formation of ZnO-CuO nano-hetero junctions. Saravanan *et al.* [64] studied the photocatalytic degradation of organic dyes such as methylene blue and methyl orange in the presence of ZnO nanorods and ZnO/CuO nano-composite based catalysts under visible light irradiation. The irradiated samples were analyzed for total organic carbon and chemical oxygen demand. Basahel *et al.* [65] synthesized nano-sized ZrO₂ powders with near pure monoclinic, tetragonal and cubic structures by various methods. They were used as catalysts for photocatalytic degradation of methyl orange dye. Among these, m-sample shows a higher degradation activity of methyl orange than other two. The acid red G and rhodamine B dyes present in water can be decontaminated in an effective way by the photocatalytic degradation under visible light irradiation (> 420 nm) with hierarchically structured α -Fe₂O₃/Bi₂WO₆ composite, which exhibits strong adsorption capability and a higher visible light photocatalytic activity than pure Bi₂WO₆ [66]. Li *et al.* [67] performed the electrically assisted photocatalytic degradation of acid orange 7 with β -PbO₂ electrodes modified by TiO₂. It results in effective photocatalytic degradation due to the combination of photocatalysis and externally applied electric field. Ullah & Dutta [68] found that basic aniline dye and methylene blue organic contaminants in water undergo photocatalytic degradation by manganese-doped ZnO and undoped ZnO photocatalysts under visible light irradiation with tungsten bulb. Higher photodegradation efficiency of ZnO:Mn²⁺ was reported by them than with undoped ZnO in bleaching the organic contaminant especially methylene blue.

Pharmaceutical and personal care products: The rapid increase in the population results in the increased demand of pharmaceuticals now-a-days. Pharmaceutical products and their wastes play a major role in the degradation of environment. These drugs have positive as well as negative consequences on different environmental components including biota in different ways. Many types of pharmaceutical substances have been found out with significant concentrations through different advanced instrumental techniques in surface water, subsurface water, ground water, domestic wastewater, municipal wastewater and industrial effluents [69]. This causes adverse effect on human beings [70]. Improper treatment of pharmaceutical waste causes harmful effects on living organism, including morphological, metabolic and sex changes in aquatic species, induction of antibiotic resistance in aquatic

pathogenic microorganism and interruption of biodegradation activities in sewage treatment plants [71]. Cardoso *et al.* [72] have summarized that human and veterinary active pharmaceutical ingredients (APIs) are involved in contaminants of surface water, ground water, effluents, sediments and biota. The untreated or partially treated effluents were discharged to drinking water sources in which different class of pharmaceutical compounds like contraceptive, analgesic, antidepressant, antihypertensive, antibiotics, steroids have been detected from mg/L to μ g/L range [73]. Oaks *et al.* [74] shown that population decline of white-baked vulture by > 95% was due to consumption of water contaminated with diclofenac medicine. So, it is required to treat such contaminated water. Advanced oxidation processes (AOPs), in particular UV/TiO₂, have potential for wastewater treatment [75,76]. The presence of fluoroquinolone antibacterials such as ciprofloxacin, danofloxacin, erofloxacin, levofloxacin, marbofloxacin and moxifloxacin in untreated water was investigated. This water was undergone photolytic and photocatalytic treatment by TiO₂ photocatalyst under natural sunlight for the remediation of pollutants at the μ g L⁻¹ levels despite the presence of other non-target matrix constituents [77]. Elmolla & Chaudhuri [78] observed the complete degradation of other antibiotics including amoxicillin, ampicillin and cloxacillin contamination in water by UV/TiO₂ and UV/H₂O₂/TiO₂ photocatalysis. Among environmental pollutants, pharmaceuticals and active ingredients in personal care products, both human and veterinary, including not just prescription drugs and biologics, but also diagnostic agents, nutraceuticals, fragrances, sunscreen agents, *etc.* were also observed [79]. China is one of the largest producers and consumer soft pharmaceutical and personal care products (PPCPs) across the globe. This resulted in PPCP contamination in different environmental media of China [80,81]. Lin *et al.* [82] investigated the photocatalytic treatment of diluted wastewaters containing emerging paraben pollutants in TiO₂ suspension under UV irradiation at pH 9. It was reported that heterogeneous photocatalysis using carbanaceous-TiO₂ is an effective methodology to remove the presence of PPCP from natural and wastewater [83].

Inorganic pollutants: The inorganic substances including fluoride, arsenic, mercury, cyanide, chromium, lead, *etc.* can get into water bodies through industrial waste products contaminate the water resources to a greater extent. It was reported that if the emission of inorganic substances into the environment continue at the current rate, it will result as a global problem [84]. Heterogeneous photocatalysis is an effective technology for the removal of inorganic compounds from wastewater.

Fluoride: The source of fluorides includes pharmaceutical products, toothpaste, insecticides, fertilizers, disinfectants *etc.* These substances enter into the water bodies and cause many health issues in human beings. The fluoride in drinking water causes dental and skeletal fluorosis [85]. The presence of fluoride in drinking water was investigated in many states in India [86]. So, it is required to purify such contaminated water having excess fluoride content. Merino *et al.* [87] observed that the advanced oxidation processes including photocatalysis is an effective way of treating water contaminated with fluoride as perfluoro-

alkyl and polyfluoroalkyl substances, since they are identified as toxicants, endocrine disrupters and possible carcinogens.

Arsenic: The arsenic exposure to human is from drinking water, food, cigarettes, cosmetics, air, *etc.* [88]. It was reported that drinking water is the largest source of arsenic poisoning worldwide, which can adversely influence human health. Arsenicosis, a disease caused by arsenic contamination in drinking water [89] and other effects of inorganic arsenic include skin rashes, neurological effects, hypertension, peripheral vascular disease, cardiovascular disease, respiratory diseases, diabetes, mellitus and malignancies including skin cancer [90]. The skin is quite sensitive to arsenic and skin lesions are some of the most common and earliest nonmalignant effects related to chronic arsenic exposure. So, it is necessary to treat the arsenic contaminated water. Photocatalytic degradation with different photocatalysts such as iron oxide, zinc oxide, TiO₂ and zirconia was reported [91]. Hu *et al.* [92] explained about the removal of inorganic and organic arsenic by photocatalytic degradation using TiO₂ and TiO₂ based materials. The photocatalytic degradation of arsenic by the TiO₂-ZnO composite nanostructures in the presence of UV and visible light irradiation was observed by Arabnezhad *et al.* [93]. Zhang and Itoh [94] have investigated the photocatalytic oxidation for the removal of arsenite from water using slag-iron oxide-TiO₂ adsorbent under UV light irradiation. They have found that a concentration of 100 mg L⁻¹ arsenite could be entirely oxidized to arsenate within 3 h.

Mercury: Mercury can enter into the drinking water from industries, aquatic sediments and soil. Mercury poisoning causes damage in brain functioning in adults. Also, prenatally poisoned infants exhibit a range of effects from severe cerebral palsy to subtle developmental delays [95]. Yepsen *et al.* [96] have used UVA light assisted TiO₂ heterogeneous photocatalysis for the first time in order to degrade thimerosal (sodium ethylmercury thio-salicylate) completely within 20 min. It was reported that combination of the sewage sludge carbon with TiO₂ under ultraviolet irradiation could doubled the adsorption capacity of mercury on the sewage sludge carbon and the removal rate increased to 151 g/kg compared to 87 g/kg for sewage sludge carbon only [97]. Wu *et al.* [98] have studied the photocatalytic removal of Hg⁰ (gaseous elemental mercury) using multi-walled carbon nanotubes (MWCNTs) impregnated with titanium dioxide (MWCNTs/TiO₂) in a fixed-bed reactor with the simulated flue gas. They have found that compared to the pure TiO₂, the MWCNTs/TiO₂ exhibited a higher photocatalytic removal ability for Hg⁰ that mainly due to the higher surface area, the better electronic transportation and the abundant active species such as the surface chemisorbed oxygen (O⁻) and C=O bond.

Cyanide: HCN and CN⁻ free cyanide forms are considered to be the most toxic substances due to their high metabolic potential [99]. Cyanide usually gets into water through improper handling or failure during transportation [100]. Peterson & Cohen [101] have studied the effects of cyanide on brain mitochondrial cytochrome oxidase and respiratory activities in mice. The results indicated that cyanide concentrations of 10⁻⁶–10⁻⁴ M produced only a 25% inhibition of respiration state, whereas 10⁻³ M produced 80% inhibition

in mice. Chiang *et al.* [102] have studied the photocatalytic degradation of cyanide using TiO₂ modified with CuO. They have found that the rate of photooxidation of cyanide assisted with the doped catalyst was improved slightly at 0.10 at.% Cu. Saravy [103] have described about the synthesis of TiO₂ nanoparticles with maximum photocatalytic properties and their application for the treatment of cyanide in wastewater. Among the three types (anatase, rutile and a biphasic mix of rutile and anatase) of crystalline TiO₂ nanoparticles, the biphasic form of TiO₂ nanoparticles demonstrated the highest removal of cyanide. Aguado *et al.* [104] have prepared titania supported samples on different types of silica by a sol-gel method followed by hydrothermal processing. They have studied the degradation of iron(III) cyanocomplexes in the absence or presence of titania catalyst and found that the oxidation of cyanides ions to cyanate species is significantly enhanced in the presence of the catalyst in which mesostructured SBA-15 silica used as a support. Barakat [105] observed about 78% removal of free cyanide from water by photocatalytic process by using TiO₂ photocatalyst with UV irradiation. Koohestani & Sadrnezhaad [106] have investigated the effect of adding 5-12.5 wt.% CuO to TiO₂ on photocatalytic properties of the nanocomposite TiO₂/CuO under UV irradiation in degrading methyl orange and cyanide. The highest rate of photocatalytic degradation was found in TiO₂-7.5% CuO. Alonso *et al.* [107] have studied the ozone enhanced activity of aqueous TiO₂ suspensions for photocatalytic oxidation of free cyanide ions in the near-UV region. They have found that the rate of cyanide oxidation by heterogeneous photocatalytic mechanism is enhanced by ozone. Bagabas *et al.* [108] have reported the room-temperature synthesis of zinc oxide nanoparticles in different media and their application in cyanide photodegradation. They have found that increasing the concentration wt.% of ZnO (prepared from ethanol) from 0.01 to 0.09 lead to an increase in the photodegradation of cyanide ions from 85% to almost 100% after 180 min. Ismail *et al.* [109] have reported a sol-gel synthesis of vanadia-silica for photocatalytic degradation of cyanide from solution. They have found that the optimum loading of vanadia-silica xerogel is 0.166 wt.% that give 98.5% cyanide removal efficiency after 3 h. Pala *et al.* [110] have reported the photocatalytic degradation of cyanide in wastewater using new generated potassium lanthanum titanates (K₂La₂Ti₃O₁₀, KLTO) nano-thin film photocatalyst with CeO₂ buffer layer. They have found that the maximum degradation efficiency of cyanide as 99.87% at pH of 10 and light intensity of 750 W/m².

Chromium: The chromium exists in the aquatics in two states-hexavalent Cr(VI) and trivalent Cr(III), in which Cr(VI) species are known to be toxic and carcinogenic than other state. The presence of hexavalent chromium in wastewater is a potential hazard to aquatic lives and humans. Chromium(VI) wastes, which are generated by the process including rinsing of metals, anodizing, electroplating, dip solutions and bright dips are exposed to water and gets contaminated [111]. Cr(VI) exposure causes lung cancer and cancers in other tissues of the gastrointestinal and central nervous systems. Also, it was reported that the induction of skin tumors in mice by chronic drinking water exposure to hexavalent chromium in combi-

nation with solar ultraviolet light [112]. High level exposure of Cr(VI) causes liver and kidney damages, dermatitis and respiratory problems in humans and animals [113]. Joshi & Shrivastava [114] have reported the photocatalytic degradation of Cr(VI) from wastewater using nanomaterials like TiO₂, ZnO and CdS. They have found that the maximum removal of Cr(VI) is observed at pH 2; out of these photocatalysts, TiO₂ showed highest capacity for Cr(VI) removal than TiO₂ thin film. Wu *et al.* [115] have reported a rapid method to photocatalytically reduce the highly toxic Cr(VI) to Cr(III) by a graphene oxide (GO) photocatalyst utilizing renewable sunlight or visible light. They have reported that the photocatalytic reactivity of GO is comparable with or superior to that of P25 TiO₂ under sunlight or visible light irradiation and is among the best in existing photocatalytic Cr(VI) reduction systems involving carbon-based nanomaterials.

Lead: Lead can reach a water source through aquatic, atmospheric and terrestrial ways [116]. The lead toxicity causes many dysfunctions in human body including hematological, gastrointestinal and neurological and severe exposure carries chronic nephropathy, hypertension and reproductive impairment [117]. The lead removal from water is generally performed by the precipitation process or carbonate or hydroxide with/without coagulation. Heterogeneous photocatalysis is an effective method for the degradation of Pb(II) from wastewater [118]. Mishra *et al.* [119] have observed the photocatalytic reduction of lead by using 10 wt.% silica mixed titania and 10 wt.% zirconia mixed titania, in which, zirconia mixed titania is the potential catalyst for the visible light reaction. The complete removal of Pb²⁺ was reported in 1 h of reaction using synthesized catalysts in presence of a scavenger such as sodium formate.

Microbial pollutants: Chlorination is a common water disinfection method especially to kill microbial pathogens, but chlorine in water causes asthma [120], dermatitis [121] and bladder cancer [122]. Heterogeneous photocatalysis is considered as an assured substitutional technique for the disinfection of water with least risk of harmful consequences which was observed by Mahmood *et al.* [123]. The first application of TiO₂/Pt (platinum-loaded titanium oxide) photocatalyst for the photochemical sterilization of microbial contaminants in water was reported by Matsunaga *et al.* [124]. *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli* (10³ cells/mL) were completely sterilized by this technique under metal halide lamp irradiation for 60-120 min. Reddy & Kim [125] have reported a survey about TiO₂ materials in the disinfection of a wide range of environmentally harmful microbial pathogens (*e.g.* bacteria, fungi, algae and viruses) in aqueous media.

Bacteria are considered to be the effective indicator of water pollution than other microbes. In bacteria, *Escherichia coli* is the most common microbial contaminant in water and causes many health issues including typhoid, dysentery, cholera and gastroenteritis [126]. It was reported that *E. coli* survives in drinking water for about 4 to 12 weeks, depending on environmental conditions (temperature, microflora, *etc.*). Many studies have been carried out to evaluate the photocatalytic property of many photocatalysts for the effective disinfection of bacteria (*E. coli*). An effective treatment of an extensive range of biolo-

gical species by TiO₂ photocatalyst was studied by McCullagh *et al.* [127]. Alrousan *et al.* [128] have reported that the photocatalytic and photolytic inactivation rates of *Escherichia coli* using immobilized nanoparticle TiO₂ films were found to be significantly lower in surface water samples in comparison to distilled water. Sun *et al.* [129] have investigated the total mineralization of the bacteria to the extent of death and cell-mass inactivation using a TiO₂-Fe₂O₃ membrane photocatalytic oxidation reactor. During this process, *E. coli* could be further mineralized into CO₂ and H₂O. Many studies have shown that the enhancement in photocatalytic efficiency by metal doping. Dunlop *et al.* [130] have carried out photocatalytic degradation of bacterial pollutant (*E. coli* K 12) in drinking water using TiO₂ electrodes.

Sunada *et al.* [131] have investigated the bactericidal activity of copper-deposited titanium dioxide thin film (Cu/TiO₂) under very weak ultraviolet (UV) light illumination. In the process, the survival rate of both copper resistant cells under dark conditions and in very weak UV light was examined. In copper-resistant cells, there was no decrease in survival rate, whereas in weak UV light (1 μW/cm²), the decrease in survival rate observed, which show photocatalytic bactericidal activity. Wang *et al.* [132] have reported that outer membrane of *E. coli* is removed completely in the presence of ZnO nanowires under UV irradiation and the cells became twisted shapes without a mechanically strong network. Hu *et al.* [133] investigated the photocatalytic disinfection of pathogenic bacteria in water systematically with AgI/TiO₂ under visible light (λ > 420 nm) irradiation. The catalyst was found to be highly effective in killing *E. coli* and *S. aureus*. Zhang *et al.* [134] have observed an effective photocatalytic disinfection of *E. coli* K-12 by using AgBr-Ag-Bi₂WO₆ nanojunction system as a catalyst under UV light irradiation. The visible light driven (VLD) AgBr-Ag-Bi₂WO₆ nanofunction could completely inactivate 5 × 10⁷ cfu mL⁻¹ *E. coli* K-12 within 15 min. The chemical treatment of cyanotoxins in water such as chlorination and ozonation can produce productive oxidation reactions. But, the oxidation of cyanobacterial toxins produces harmful byproducts. In recent years, many studies have reported in successive photocatalytic degradation of cyanotoxins. Senogles *et al.* [135] have examined the effectiveness of two brands of TiO₂ under UV photolysis for the degradation of cylindrospermopsin. Results indicated that TiO₂ is an efficient photocatalyst for cylindrospermopsin degradation. Titanium dioxide (TiO₂), brand Degussa P-25 was found to be more efficient than the alternate brand Hombikat UV-100. The heterogeneous photocatalytic degradation of the blue green algal toxin, microcystin-LR in a natural organic-aqueous matrix was examined by using TiO₂ photocatalyst. It results in a rapid degradation of toxin at acid pH range 3.5 in the presence of light and TiO₂, which was carried out by Feitz *et al.* [136]. Antoniou *et al.* [137] have observed the photocatalytic degradation occurred at 4 sites of the microcystin-LR with immobilized TiO₂ photocatalyst at neutral pH. A higher rate of photocatalytic degradation of microcystin-LR in water by non-metal doped TiO₂ nanoparticle under visible light irradiation was investigated by Pelaez *et al.* [138]. They have developed N-F co doped TiO₂ photocatalyst for degradation

under acidic condition (pH 3.0 ± 0.1) and observed highest photocatalytic activity than TiO₂ nanoparticles with only fluorine or nitrogen doping.

Conclusion

Because of increase in population, urbanization, modernization, etc. the water bodies undergo chemical pollution severely which may influence the survival of animals, birds, plants and even humans. Several materials viz. organic pollutants, such as pesticides, herbicides, fungicides, insecticides, nematicides, dyes, pharmaceutical and personal care products, which cause greater level of water pollution. In case of inorganic pollutants, substances like fluoride, arsenic, mercury, cyanide, chromium, lead, etc. can get into the water bodies through industrial waste and contaminate the water resources to a greater extent. Apart from the above, the pollution of water by microbes is a great threat to the survival of living organisms. From the literatures discussed, it is found that photocatalysis using suitable photocatalysts is an effective method for the effective degradation of water contaminants, especially, organic, inorganic and microbial contaminants from water. However, still the efficiency of the photocatalysis reactions has to be further improved by suitable methods to eradicate the environmental pollution completely from water bodies.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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