

REVIEW

Inorganic Metal Oxides and Multi-Component Nanocomposites Based Photocatalysts for the Superior Degradation of Pollutants from Water

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Water is a fundamental and indispensable resource for all living organisms, serving as a vital contribution from the natural world that enables the survival of every living creature. Unfortunately, modern human activities have resulted in severe pollution of water sources. Many industrial units like textile mills, pharmaceutical units, mines, paper mills, dyeing units, sugar industries, leather purifying units, electroplating plants, fine chemical units, oil refineries, *etc.* produce huge amount waste products in the form of toxic chemicals and pollutants every day and enter the water bodies without proper treatment. Various techniques are available to purify the polluted water by eliminating the toxicity of pollutants; some of them are reverse osmosis, electrode ionization, ion exchange, submicron filtrations, *etc.* Among all these water treatment procedures, photocatalysis is found to be most versatile, low cost and environmentally benign technique. In this review, a prime focus is given on the performance of different photocatalysts based on ZnO, CuO, NiO, SnO₂, MgO, multicomponent metal oxides and their composites in degrading and removing unwanted impurities present in polluted water. The importance of using metal oxide based photocatalysts in treating the polluted water is also discussed.

Keywords: Water pollutants, Degradation, Photocatalysis, Metal oxides, Nanocomposites.

INTRODUCTION

Pollution refers to the introduction of hazardous substances or materials into the natural environment. These hazardous compounds are commonly referred to as pollutants. The majority of pollutants are introduced into the environment as a consequence of human activities, primarily through manufacturing activities, which leads to the degradation of water, air and land quality. Air pollution is a result of the growth of industrialization, automobiles and the burning of remnant gases [1]. Similarly noise pollution, both inside and outdoors, has been identified as a severe health risk, with growing negative impacts on foetus, newborns, children, teenagers and adults. In all age groups, including the foetus, noise-induced hearing loss and non-auditory deleterious consequences are being detected more often [2]. Noise pollution results in physiological disturbances and auditory consequences in people [3]. The loss of soil productivity due to the presence of soil contaminants is known as

soil pollution. Soil contamination may be due to the presence of variety of contaminants like abandoned food, bottles, organic manure, radioactive waste, fertilizers, chemicals, pesticides, leather products, tin cans, paper, clothing, plastics and dead bodies [4].

Water is a crucial natural resource for all the human beings. People can survive without food for a short while, but no one can survive without water. Human activities have an impact on water quality, which is deteriorating because of various reasons, like, population expansion, urbanization, agricultural development and others [5]. Activities which are responsible for water pollution are depicted in Fig. 1. The discharge of diverse harmful industrial effluents into rivers results in the contamination of water, so significantly impacting the process of irrigation. The intake of contaminated water poses significant risks to human health [6]. The primary cause of water pollution is the release of undesirable contaminants into aquatic environments [7]. The water pollutants can be classified as metals (such

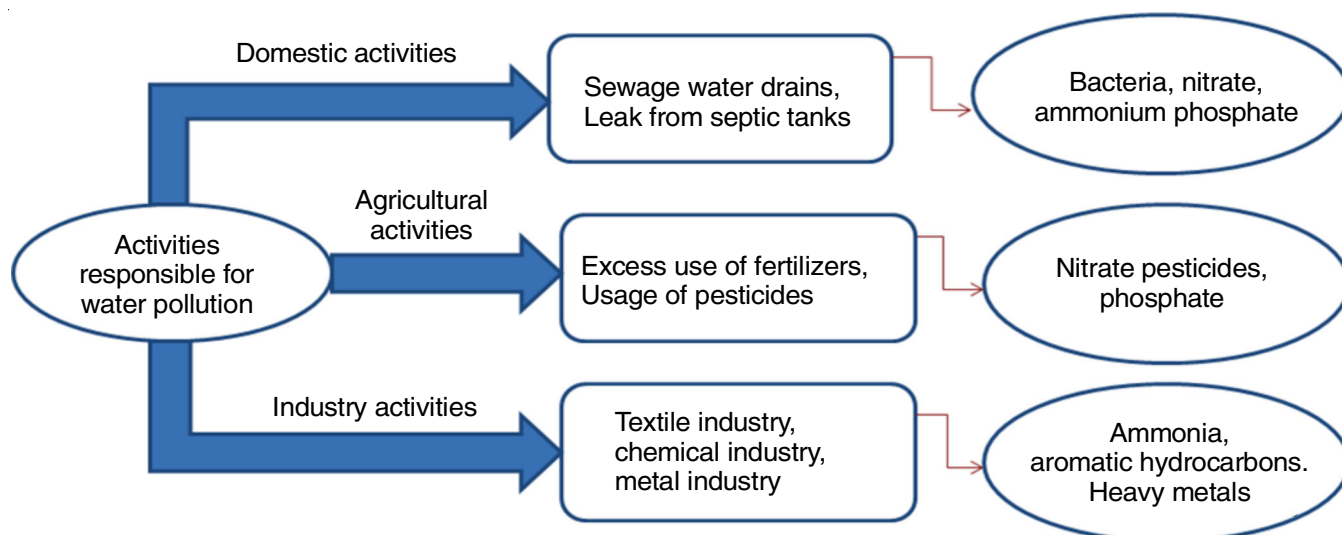


Fig. 1. Several activities responsible for water pollution

as zinc, cadmium, lead, *etc.*), nutrients (nitrate and phosphate compounds), oil based products, toxic organic wastes (formaldehyde and phenol), farm manure and domestic sewage, detergents, heat, harmful gases, *etc.* [8].

There are several technologies available to purify the water easily. The waste water will go through the following stages, *viz.* beginning, equilibrating, halting and rinsing in dairy industries for initial purification. After initial treatment, the partially purified water will be subjected to reverse osmosis technique to improve the quality of water [9]. Capacitive deionization is a modern approach which is used for separating and recovering salt ions and heavy metal ions from polluted water [10]. Electroplating effluent solution containing Cr, Ni, Zn and Cu was treated effectively using electrocoagulation technique using Al electrodes [11]. Novel water treatment technologies, such as electrochemical advanced oxidation processes (EAOPs), have developed as effective methods for eliminating of a wide range of organic contaminants [12]. Electrocoagulation (EC) and electrofiltration (ECF) technologies are frequently utilized in order to flocculate impurities and treat contaminants without the use of any chemical coagulants [13,14].

Photocatalysis-based water treatment has recently attracted a lot of attention, which offers a number of benefits, such as operating at standard temperatures and atmospheric pressure, being inexpensive, not producing any secondary waste and being easily accessible [15]. A photocatalyst is a substance which can absorb light and produce electron-hole pairs. This will allow the reactants to undergo chemical changes and replenish its chemical composition during such interactions [16]. Since 1972 several studies, research on application of photocatalysis in numerous fields, such as water/air purification, water splitting, CO₂ reduction and N₂ fixation, has been accelerated. Under normal conditions, the photocatalysis can oxidize inorganic pollutants to innocuous compounds while eliminating organic contaminants in wastewater into carbon dioxide, water molecule or other small compounds [17,18]. Most of the workers are now interested in improved methodology of photocatalytic degradation involving both non-spontaneous and spontaneous

reactions in presence of light. However, only a small percentage of photocatalysts were shown to be fully competent to decompose organic contaminants. Numerous photocatalyst preparation methods, including doping, morphological modification, metal loading and coupling heterojunction, have been investigated and tried in the last 10 years [19]. In this review article, the main focus is given on the performance of different photocatalysts based on metal oxides and multicomponent metal oxide based nanocomposites in eliminating the hazardous contaminants present in effluents.

Primary metal oxide based materials: Most of the metal oxides can be used as photocatalysts mainly due to their promising electrical characteristics, light captivation qualities and charge transportation features. They can produce charge carriers when induced with the necessary amount of energy [20]. The metal oxides such as V₂O₅, Cr₂O₃, CeO₂, SnO₂, ZnO and TiO₂ were tend to exhibit excellent photocatalytic properties. In these metal oxides, light absorption can cause charge separation which may result in the formation of positive holes and because of this effect, organic molecules can be oxidized easily [21]. It was reported that heterogeneous photocatalysis is a very effective technique in converting a variety of different contaminants into biodegradable chemicals which in turn mineralize them as harmless carbon dioxide and water [22,23]. Metal oxides based on ZnO, WO₃, Fe₂O₃ and Bi₂O₃ have received special attention because of their excellent physico-chemical characteristics [24].

Zinc oxide photocatalysts: One of the most effective primary photocatalysts is zinc oxide (ZnO). It was reported that the zinc oxide has high photosensitivity and wide gap which results in efficient degradation of various pollutants present in water [25]. ZnO nanoparticles prepared by flame spray pyrolysis using oxygen gas as oxidizer and LPG as fuel was effective in degrading amaranth dye (95.3%) under sunlight for 75 min [26]. ZnO can exhibit in several morphologies as well. Methyl orange can be effectively broken down by ZnO nanorods. Methyl orange endured a 3 h UV exposure that degraded it by up to 95% [27]. ZnO nanoparticles were employed as a photocatalyst

to break down rhodamine B dye with an efficiency of 95.41% within 160 min with an ideal catalyst load of 0.2 g. Similarly, sol-gel approach is another preferable approach in preparing ZnO nanostructures for the elimination of hazardous pollutants from wastewater [28]. *Rosmarinus officinalis* leaf extract was used to synthesize two types of ZnO nanoparticles at 80 °C (ZnO-80) and 180 °C (ZnO-180). According to photocatalytic experiments, ZnO-80 and ZnO-180 degraded methylene blue by 99.64% (45 min) and 98.82% (60 min), respectively in sunlight [29]. *Abelmoschus esculentus* Linn. leaves can be effectively used to prepare ZnO nanoparticles using a green route at room temperature. The organic dyes were degraded easily using green synthesized ZnO nanoparticles under UV light [30]. The degradation of textile dyes in presence of green synthesized ZnO nano-photocatalysts is presented in Table-1.

Copper oxide photocatalysts: Copper(II) nitrate trihydrate was used as a precursor salt in a chemical precipitation process to prepare CuO nanoparticles, which have an energy band gap of roughly 1.76 eV. Under visible light irradiation and in presence of CuO based photocatalysts, reactive black 5 (RB5) exhibited largest decolorization compared to methylene blue and acid yellow 23 dyes [31]. Simple solvothermal process was also used to prepare bud-shaped CuO and cubic Cu/Cu₂O/CuO nanocrystalline materials. It was interesting to observe that after 120 min, Cu/Cu₂O/CuO nanoparticles eliminated 78% of methylene blue dye in the presence of H₂O₂ [32]. A simple green route was adopted to prepare the CuO nanoparticles using a biofunctional reducing material, *Rhizome* extract of *Bergenia ciliata*. In presence of sunlight, the prepared CuO nanoparticles were used to degrade methylene blue and methyl red dyes with the % degradation efficiency of 92% and 85%, respectively under the irradiation of sunlight for 135 min [33]. A one-pot bio-mechanochemical method with *Seriphidium oliverianum* leaf extract was used effectively to produce CuO nanoparticles. The produced CuO nanoparticles were used as photocatalysts to decolorize methyl green and methyl orange dyes with the degradation efficiency of 65% under sunlight after 60 min [34]. Sonication method was used efficiently to prepare transition metal viz., Ni, Zn and Fe doped copper oxide nanocrystalline materials. Among the samples, Zn doped CuO exhibited excellent performance (63%) in degrading methylene blue dye under visible light after 60 min [35].

Nickel oxide photocatalysts: The chemical reduction method was used to prepare NiO nanoparticles and nickel oxide/nanoclay nanocomposite materials, which were then used to degrade orange II dye in water medium in the presence of UV

light after 20 min exposure with degradation efficiency of 93% and 96%, respectively [36]. NiO nanoparticles were fabricated by sol-gel routes using *okra* plant extract. They were able to degrade methylene blue dye completely at pH under optimal conditions in UV light for about 300 min [37]. NiO substituted *Nephelium lappaceum* L. peel extract photocatalyst exhibited performance in degrading rhodamin B dye with % degradation efficiency of 92.3% under UV light for 180 min [38]. Alternatively, the hydrothermal synthesis was used to prepare NiO nanobelts and the synthesized NiO nanobelts were used as efficient photocatalysts in degrading different dye molecules such as methylene blue, methyl orange, crystal violet and rhodamine B dyes after irradiating in the presence of UV light for 140 min. The photodegradation efficiency was found to be 82.7%, 79.1%, 76.7% and 89% for eliminating methylene blue, methyl orange, crystal violet and rhodamine B dyes, respectively [39]. Recently, Rashid *et al.* [40] utilized D-sorbitol as a capping agent and olive tree leaves as a reducing agent to prepare NiO nanoparticles as photocatalysts by green synthesis route for removing methyl orange and methylene blue dyes with the degradation efficiency of 96% (after 100 min irradiation) and 88% (after 160 min irradiation).

Tin dioxide photocatalysts: The prominent textile dyes, such as Congo-red and methylene blue dyes were also successfully degraded in the presence of tin oxide nanoparticles under ultrasonication and UV light. However, it was found that the degradation characteristics got increased under ultrasonication [41]. Hydrothermally synthesized SnO₂ nanoparticles were effective in degrading eosin dye completely within 18 min under UV light irradiation [42]. SnO₂ nanoparticles synthesized *via* a simple route were also found to be highly effective in removing rhodamine B and methylene blue dyes under UV light within 270 and 50 min, respectively [43]. The sol-gel prepared SnO₂ nanoparticles were also very active in degrading the textile dyes, such as rhodamine B, methyl orange and methylene blue dyes under UV light irradiation. The removal efficiency for methylene blue was higher (93%) within 90 min [44].

Luque *et al.* [45] synthesized SnO₂ nanoparticles using *Citrus aurantifolia* as reducing agent and using these nanoparticles, methylene blue dye was degraded effectively (96%) under UV light for 120 min. However, hydrothermally synthesized SnO₂ nanoparticles can be more effective in eliminating methylene blue dye (88.88%) under UV light within 30 min [46]. Their degradation time was highly influenced by the particle size of the synthesized SnO₂ nanostructures and they can exhibit 100% degradation for methylene blue dye under

TABLE-1
PHOTO DEGRADATION OF TEXTILE DYES IN PRESENCE OF GREEN SYNTHESIZED ZnO NANO-PHOTOCATALYSTS [Ref. 30]

Time (min)	Methylene blue dye degraded (%)	Methyl orange dye degraded (%)	Time (min)	Methylene blue dye degraded (%)	Methyl orange dye degraded (%)	Time (min)	Methylene blue dye degraded (%)	Methyl orange dye degraded (%)
30	1.2	1.4	210	20.5	22.1	390	66	68
60	4.3	4.7	240	28.5	30.5	420	78	75
90	6.4	6.6	270	32.4	36.4	450	88	84
120	7.7	7.8	300	40	45	480	90	90
150	12.5	12.8	330	48	58	510	95	94
180	16.6	16.8	360	56	66	540	96	96

UV light [47]. Iron doped SnO₂ nanoparticles were synthesized by simple hydrothermal method. They were effective photocatalysts in presence of H₂O₂ in degrading crystal violet dye with elimination percentage of 98% under visible light illumination [48].

Magnesium oxide photocatalysts: Magnesium oxide nanoparticles were prepared by a simple green method using a reducing agent derived from *Camellia sinensis* (tea leaves) and then they were used as photocatalysts to degrade methylene blue dye almost completely (~97%) under UV light within 120 min [49]. MgO nanoparticles loaded with activated carbon can also be effectively utilized to remove methyl orange dye (99.63%) within 60 min. The methyl orange dye removal was accelerated by artificial neural network at 40 °C [50]. *Kappaphycus alvarezii* extract was used as a stabilizer during the single-step co-precipitation method of fabricating MgO nanoparticles. In presence of visible light, MgO nanoparticles exhibited significant photocatalytic activity for the elimination of the organic dyes. The experimental data was consistent with first-order kinetics and the photocatalysis carried out with the MgO nanoparticles led to the degeneration (>95%) of rhodamine B and methylene blue dyes [51]. A quick and affordable precipitation technique was also applied to synthesize MgO nanoparticles as reported by Karthikeyan *et al.* [52]. The prepared materials were used as photocatalysts in degrading (97.08%) methyl red dye efficiently. Algethami *et al.* [53] synthesized MgO nanoparticles using L-arginine and glutamine as fuels *via* combustion method. They were used as photocatalysts to remove orange G dye under UV light illumination for 120 min. The percentage degradation was found to be 96.60% and 92.30%, respectively by the samples using glutamine and L-arginine as fuels.

Calcium oxide photocatalysts: Calcium oxide and calcium oxide/carbon (CaO/C) photocatalyst materials were produced through thermal decomposition of eggshell and coffee wastes. When they were used as photocatalysts in removing methylene blue dye, CaO/C exhibited better degradation rate (99.76%) than that of CaO (88.04%) [54]. Commercial calcium oxide was utilized as photocatalyst for the elimination of indigo carmine dye at pH 9 to 12 in the presence of short UV light (at 254 nm), long UV light (at 365 nm) and visible light (using 8 W lamps). The percentage degradation of indigo carmine dye was found to be 100% at a pH of 12 between 90 to 150 min using the above three light sources [55]. Commercial CaO was used as photocatalyst to eliminate methylene blue dye in presence of visible light. The photodegradation was studied by modifying the pH, amount of catalyst, light intensity and the concentration of dye. Further, the COD level of the dye solution was reduced to 60% after the photocatalytic degradation [56]. CaO nanoparticles were also prepared by an environmentally benign technique using *Crataegus pontica* C. Koch extract as a stabilizing and green reducing agent and the prepared materials were to degrade methylene blue dye with 98.99% in presence of sunlight [57]. Vanthana Sree *et al.* [58] prepared CaO nanoparticles from eggshells waste by using heat treatment method and then they were used as photocatalyst to degrade methylene blue and toluidine blue dyes within 15 min at pH 9. Calcium

oxide nanoparticles were also used to degrade indigo carmine in 50 min under UV light as reported by Nandiyanto *et al.* [59].

Multicomponent metal oxide based photocatalysts: The photodegradation of dye mixtures by using multicomponent metal oxides such as ZnO-SnO₂ nanocrystalline materials was successfully accomplished by Dlugosz *et al.* [60]. The removal efficiencies of several dyes, *e.g.* rhodamine B, methylene blue, methyl orange, trypan blue and quinolone yellow dye were found to be 72.69%, 76.44%, 77.00%, 62.43% and 92.46% after running the processes for 60 min under UV light. Siwinska-Ciesielczyk *et al.* [61] synthesized binary and ternary photocatalysts based on titania, zirconia and/or silica *via* sol-gel route and then they were successfully used to degrade rhodamine B dye under UV-visible illumination. It was found that crystalline structure of the photocatalysts and the pH of the reaction mixture can exhibit strong influence in the degradation characteristics of the dye molecule. Recently, Azimifar *et al.* [62] developed a membrane based on Sb₂O₃/CuBi₂O₄ (Sb₂O₃/CBO) nanocomposite to degrade methylene blue and acid blue 25 dyes when exposed to visible light. The photocatalytic dye removal efficiency was found to be 94.6% for 10% Sb₂O₃/CuBi₂O₄ nanocomposites.

Nanocomposite based photocatalysts: *Plumbago auriculata* leaf extract (PALE) was utilized to prepare ZnO nanoparticles and silver doped ZnO nanoparticles. Among the samples, the nanocomposite with a composition of ZnO doped AgNPs resulted in the maximum photodegradation (95.7%) of methylene blue dye under UV light [63]. The chemical reduction method was employed to synthesize silver nanoparticles from *Gongura* leaves. On the other side, ZnO nanorods were prepared by simple hydrothermal route and then appropriate quantities of silver nanoparticles and ZnO nanorods were mixed using electrical grinder for 3 h to synthesize 5% silver nanoparticles containing ZnO nanocomposites. They were used as photocatalysts to degrade methylene blue dye (99.21%) in the presence of UV light for 75 min [64]. Recently, Dharmana *et al.* [65] hydrothermally synthesized Cu²⁺-doped ZnO-SnS nanocomposites and they were as photocatalysts to degrade methylene blue dye upto 97% in presence of solarlight under 2 h.

Khalid *et al.* [66] prepared cobalt ferrite and ZnO decorated graphene nanocomposite by sonochemistry route, which was found to be effective to degrade methylene blue dye upto 98% under solar light within 15 min. Zayed *et al.* [67] synthesized TiO₂/NiO nanocomposites *via* hydrothermal route and was successfully applied to degrade 99.5% of methylene blue dye within 45 min of exposure under UV light. Under the same conditions, pure TiO₂ nanoparticles degraded only 73% of methylene blue dye. Similarly, Elashery *et al.* [68] synthesized MgO nanoparticles and MgO-bentonite nanocomposite materials hydrothermally. They were used as to decompose crystal violet dye under UV irradiation for about 130 min. Fatimah *et al.* [69] synthesized nickel nanoparticles-impregnated biochar from palm leaves as an active photocatalytic material for the oxidation of methyl violet dye. The obtained degradation efficiency value was found to be 99% within 30 min. for methyl violet dye having the concentration of 10-80 ppm. Alshaimi *et*

al. [70] synthesized CaO nanoparticles by heat treatment of egg shells at high temperatures. The Ag@CaO composite was prepared by the simple heat treatment of CaO with silver oxalate at 200 °C. This composite was very effective in degrading (~99.21%) indigo carmine dye in presence of sunlight. Using ion exchange process, Abdelkader *et al.* [71] prepared SrO-CuBi₂O₄ nanocomposites and successfully decolourized Congo red dye with 97.22% within 220 min in presence of UV-A light. The photocatalytic activity of different metal oxides and multicomponent metal oxide nanocomposite materials is presented in Table-2.

***g*-C₃N₄ based Photocatalysts:** The *g*-C₃N₄ may be a prime option for coupling with other functional materials to improve the performance because of its distinctive electronic structure. The *g*-C₃N₄-based nanocomposites have been extensively used in the photocatalytic degradation, supercapacitors, disinfection, *etc.* [86]. One-step thermal polymerization of zinc carbonate basic dehydrate and urea resulted in the formation of *g*-C₃N₄ and ZnO nanocomposite materials. The composite with the composition GCN-Zn_{0.4} has resulted in better photodegradation efficiency (90%) within 120 min under 200 W tungsten lamp [87]. Peng *et al.* [88] prepared *g*-C₃N₄-Cu₂O nanocomposite materials using an alcohol-aqueous based chemical precipitation method, which were very effective in degrading acid orange-II (93.7%) under visible light. Lu *et al.* [89] prepared CaCO₃/*g*-C₃N₄ nanocomposite materials using calcium carbonate and melamine as precursor materials *via* simple facile calcination method. The material as photocatalyst successfully degraded the crystal violet dye under visible light

with a higher photo-degradation efficiency of 76% than CaCO₃ (23.2%) and *g*-C₃N₄ (21.6%). Alternatively, Fan *et al.* [90] prepared *g*-C₃N₄/MoS₂ nanocomposite material by using ultrasonication. The nanocomposite with a mass ratio of 1:8 (*g*-C₃N₄/MoS₂) was found to be very effective in eliminating rhodamine B dye under visible light with the photo-elimination efficiency of 99.6%. Similarly, Michalska *et al.* [91] prepared TiO₂ and melam/*g*-C₃N₄ nanocomposites with the incorporation of silver nanoparticles as efficient photocatalysts in removing acid orange 7 dye under UV and visible lamps. It was found that melam/*g*-C₃N₄ nanocomposite with 1.0 and 0.5 wt.% of silver resulted in the highest photodegradation efficiency of 98% in eliminating acid orange 7 dye under visible light. The details of the different *g*-C₃N₄ based photocatalytic materials and their degradation performance is presented in Table-3.

Doped oxides and doped oxide nanocomposites as photocatalysts: Chemical precipitation technique was used to prepare ZnO, Ag and Cu doped ZnO nanorods. These nanorods were used to prepare *meso-tetrakis*-(4-sulfonatophenyl)porphyrin (TPPS₄) immobilized ZnO (TPPS/ZnO) nanocomposite materials. They were used as photocatalysts in eliminating methylene blue dye under visible and UV light exposure. The TPPS/ZnO nanocomposite materials revealed the best performance under visible light than the other photocatalysts [100]. Mirzaeifard *et al.* [101] prepared sulphur doped ZnO nanoparticles by the hydrothermal method. Among the samples, a 0.5 wt.% sulphur doped ZnO nanoparticles were able to eliminate 100% rhodamine B dye under UV light within 90 min. Recently, Yang

TABLE-2
PHOTOCATALYTIC ACTIVITY OF METAL OXIDE AND MULTICOMPONENT METAL OXIDE NANOCOMPOSITE MATERIALS IN ELIMINATING METHYLENE BLUE DYE

Photocatalyst	Concentration of methylene blue	Light source	Time (min)	Degradation (%)	Ref.
ZnO/Eu ₂ O ₃ /NiO	5 ppm	Sunlight	150	98.0	[72]
S-ZnO NPs	20 μM	Sunlight	45	61.5	[73]
N/La-ZnO	15 ppm	Sunlight	60	97.0	[74]
ZnO-SiO ₂	9 ppm	Sunlight	90	97.8	[75]
ZnO NWs	10 ppm	Sunlight	4320	100.0	[76]
WO ₃ /ZnO@rGO	5 ppm	vis. 200 W	90	94.1	[77]
Ag-ZnO/GO	15 ppm	Xe 20 W × 5	180	85.0	[78]
TiO ₂ /ZnO/rGO	0.3 ppm	Xe 300 W	120	92.0	[79]
Mn-ZnO	10 ppm	UV lamp	90	60.0	[80]
rGO-ZnO	5 × 10 ⁻⁴ mol/L	Visible light	120	90.0	[81]
ZnO-Cd	3 × 10 ⁻⁵ mol/L	Xe 250 W	360	97.8	[82]
ZnO NPs	15 ppm	Hg lamp 10 W	120	90.0	[83]
Ag/ZnO	2 × 10 ⁻⁵ M	Xe 100 W	120	76.0	[84]
ZnO/AC	2 × 10 ⁻⁵ M	Hg lamp, 30 W	45	92.0	[85]

TABLE-3
PHOTOCATALYTIC PERFORMANCE OF *g*-C₃N₄-BASED NANOCOMPOSITES IN REMOVING DIFFERENT POLLUTANTS

Photocatalyst	Light source	Pollutant	Time (min)	Degradation (%)	Ref.
<i>g</i> -C ₃ N ₄ -CNTs-graphene	Visible	Phenol	60	43.0	[92]
mpg-C ₃ N ₄	300 W visible	4-Chlorophenol	60	~100.0	[93]
<i>g</i> -C ₃ N ₄ -BiVO ₄	30 W simulated sunlight	Methylene blue	70	~68.0	[94]
<i>g</i> -C ₃ N ₄	Simulated sunlight	Methylene blue	20	96.5	[95]
<i>g</i> -C ₃ N ₄ -CDs _a	300 W visible	Phenol	200	87.0	[96]
<i>g</i> -C ₃ N ₄	300 W visible	Methylene blue	300	66.0	[97]
<i>g</i> -C ₃ N ₄ -Ag-Fe ₃ O ₄	300 W visible	Tetracycline	90	88.0	[98]
<i>g</i> -C ₃ N ₄ -Fe ₃ O ₄ -BiOI	50 W visible	Rhodamine B	180	~100.0	[99]

TABLE-4
PHOTOCATALYTIC PERFORMANCE OF DOPED OXIDE NANOCOMPOSITES IN REMOVING DIFFERENT POLLUTANTS

Photocatalysts	Preparation method	Dye/Drug	Time (min)	Lamp source	Degradation (%)	Ref.
TiO ₂ -Ag	Dip coating & sol-gel spin coating	Methyl orange	60	UV-light	69.00	[109]
Nd ₂ O ₃ -doped ZnO	Hydrothermal method	Methylene blue	60	UV-light	96.00	[110]
Ag/Nd ₂ O ₃ -ZnO	Hydrothermal method	Methylene blue	30	Visible-light	98.12	[111]
Nd ₂ O ₃ -doped SnO ₂	Sol gel method	Methylene blue	240	Visible-light	93.10	[112]
Nd ₂ O ₃ -ZnO-GO (0.3% Nd)	Co-precipitation	Indigo carmine	210	Visible-light	95.00	[113]
Nd-TiO ₂ -GO (0.6% Nd)	Sol gel method	Indigo carmine	180	Visible-light	92.00	[114]
Nd-doped ZnO	Sol-gel method	Methylene blue	25	UV-light	98.00	[115]
3 mol%Ce ³⁺ -doped CuO	Sonochemical method	Methylene blue	180	Visible-light	98.00	[116]
Nd-TiO ₂ -C	Sol-gel, impregnation method	Methylene blue	160	UV-light	100.00	[117]
Nd-doped ZnO	Sol-gel method	Tetracyclin	120	Visible-light	100.00	[118]

et al. [102] synthesized zinc-based MOF [MIL-125(Zn)] via solvothermal technique. Using this, an efficient Ag doped ZnO (Ag/ZnO) was prepared as photocatalyst via pyrolysis technique for the elimination of rhodamine B (99.4%) within 20 min under UV light irradiation. Rapid combustion technique was also used to prepare titanium doped ZnO (Ti-ZnO) nanoparticles as reported by Wongrerkdee *et al.* [103]. These photocatalytic materials exhibited an excellent performance in removing methylene blue dye molecules under UV light. Masood *et al.* [104] adopted sol-gel method in order to prepare La doped CuO nanoparticles. Among the various compositions, 2% lanthanum doped CuO exhibited 80% degradation efficiency against methylene blue dye under UV visible light for 100 min. Similarly, El-Sayed *et al.* [105] prepared Nd₂O₃ doped CuO nanoparticles by simple combustion technique and they were used as photocatalysts in removing methylene blue dye in presence of visible light. Among the different compositions studied, 7.5% Nd₂O₃ doped copper oxide exhibited the highest photodegradation efficiency of 90.8% within 80 min. The degradation efficiency was raised to 99% after adjusting the pH to 10.

Siriwong *et al.* [106] used wet chemical method to fabricate iron doped CeO₂, WO₃-doped ZnO and iron doped TiO₂ nanocomposite materials. They were used as effective photocatalysts in mineralizing formic acid, oxalic acid, glucose, sucrose and methanol in presence of visible and UV light. In the same way, Kannan *et al.* [107] synthesized NiO-Ce_{0.9}Y_{0.1}O_{2-δ}-Ce_{0.9}Sm_{0.1}O_{2-δ} nanocomposite by wet chemical route. It was used as photocatalyst in eliminating congo red dye (93%) within 150 min under sunlight. Lertthanaphol *et al.* [108] fabricated metal (Ag/Pd/Cu) doped TiO₂/graphene oxide nanocomposite material as a superior photocatalyst in the photoreduction of CO₂ into ethyl alcohol by simple one-step hydrothermal synthesis technique. The photocatalytic performance of doped oxide nanocomposites in removing different pollutants is presented in Table-4.

Conclusion

Since most of the pollutants exhibit high stability towards light and temperature, lengthy breakdown processes may be required in order to eliminate them completely from water. Since the majority of water pollution is non-toxic and biodegradable, it is necessary to use effective alternative methods to remove the

remaining dangerous toxins. Among the several techniques studied for the removal of pollutants, photocatalysis is reported to be highly efficient in removing or degrading or eliminating the pollutants, such as, heavy metals, industrial wastes, textile dye molecules, drug molecules, *etc.* by using nanocrystalline metal oxides, multi-component nanocrystalline metal oxides and metal oxide based nanocomposites as effective photocatalyst materials. However, several operational factors, such as pH, degradation time, dye concentration and photocatalyst loading should be controlled suitably by trials in order to achieve 100 % elimination of pollutants from water.

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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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