Metal Oxide Nanoparticles and their Nanocomposite-based Materials as Photocatalysts in the Degradation of Dyes

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Abstract: The introduction of inorganic and organic pollutants into water bodies has become a serious issue globally. The waste streams released from the textile, plastic, leather, paper, pharmaceutical, and food industries introduce different natural and synthetic dyes into the aquatic system. Nanomaterials play a significant role in the photocatalytic degradation of dyes present in wastewater. Inorganic metal oxide nanoparticles have many improved physical and chemical properties and attracted much attention in photocatalytic activities. Dyes have been released in our aquatic bodies due to many anthropogenic activities and caused life-threatening problems. Various conventional methods were reported to remove dyes from water and wastewater; the photocatalytic method is one of the efficient and cost-effective. The present review article includes detailed information on photocatalysis, the potential of metal oxide and their composite materials as photocatalysts in the degradation of toxic dyes, and some common synthetic and characterization methods used for metal oxide-based nanoparticles.

Keywords: wastewater; dyes; photocatalytic activity; metal oxide nanoparticles; composite materials of metal oxide nanoparticles.

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1. Introduction

Nanotechnology is the practice of nano-scaled objects in different fields of science and engineering. In general, the nano-scaled objects contain particle sizes from 1 to 100 nm, and nanotechnology provides their design, synthesis, characterization, and utilization for different purposes. The nanomaterials have been designed with their highly specific and controlled physical and chemical characteristics [1]. Since the last decades, very remarkable interest has been developed to synthesize and utilize nano-scaled materials [2]. The inorganic metal oxide nanoparticles attracted great attention due to their advanced physical and chemical characteristics. Metal oxide nanoparticles were considerably utilized in medicine, material chemistry, information technology, electronics, and catalysis, energy, sensors, and environmental remediation, optical, pharmaceutical, and biological sciences. Some common applications of metal oxide nanoparticles are illustrated in Figure 1. The common metal oxide nanoparticles such as CuO, MnO2, SnO2, TiO2, ZnO, ZrO2, and CeO2 have been utilized in different fields of science and technology. The properties of magnetic metal oxide nanoparticles are generally based on their shape and sizes and the specific type of materials used in their synthesis [3-7]. The nanocomposite materials based on metal oxide nanoparticles
are of a diverse class of materials in terms of electromagnetics, physical, chemical, and other properties. The successful utilization of such nanocomposite materials in adsorption and photocatalysis is due to their large surface area, good pollutants loading capacity, a specific affinity for various contaminants, and fast kinetics. As photocatalysts, metal oxide nanoparticles and their composite materials are used to degrade non-decomposed contaminants from water and wastewater [8]. Water pollution due to inorganic and organic pollutants has become a very sensitive issue in the world. Anthropogenic activities such as urbanization, industrialization, fossil fuel combustion, and others release the inorganic and organic-based pollutants into aquatic bodies.

![Diagram showing applications of metal oxide nanoparticles](https://biointerfaceresearch.com/)

**Figure 1.** Common applications of metal oxide nanoparticles.

The dyes are used in plastic, leather, paper, pharmaceutical, food, and textile industries and ultimately released into fresh and saline water. The dyes are water-soluble organic species; dyes and their metabolites are definitely harmful to humans and other living organisms [9,10]. Due to high water solubility, they are very difficult to remove from water and wastewater. Dyes are generally used in the textile and food processing industries and released through their waste streams. In general, the waste stream of such industries contains bleaching agents, finishing chemicals, thickening agents, surface-active chemicals, metallic salts, and dyestuffs. Most dyes cause irritations, eye damage, dizziness, sweating, nausea, skin discoloration, headache, and other health problems [11-18]. Dyes may be natural or synthetic; the natural dyes are mainly derived from minerals, insects, and plants. The synthetic dyes are water-soluble, water-insoluble, and in-situ color formation. According to chemical nature, the synthetic dyes are classified into sulfur, anthraquinone, phthalocyanine, triarylmethane, and azo, whereas according to their mode of application, they may be direct dispersed, basic, reactive, and vat types [18,19]. According to the presence of chromophore, the textile dyes are categorized as nitrated, phthalain, triphenyl methyl, nitro, azo indigo, anthraquinone etc. [20]. The dye waste stream released from different industries shows high color intensity, pH, suspended solids, metallic species, and their salts and high chemical oxygen demand (COD), biological oxygen demand (BOD), and temperature [19-24]. The reported methods such as membrane filtration, oxidation, photodegradation, adsorption, biodegradation, and other physical and chemical have
been successfully used to remove dyes from aqueous solutions [10, 25-29]. The photocatalytic methods are efficient, low cost, and very effective using nano-based materials as photocatalysts [30-33]. This review article discusses detailed information of photocatalysis, the potential of metal oxide and their composite materials, some common synthetic approaches, and characterization techniques of metal oxide nanomaterials.

2. Photo-Catalysis and its Mechanism

Catalysts are generally used to speed up chemical reactions; photocatalysts are utilized to speed up chemical reactions in the presence of ultra-violet (UV) and visible lights. The photocatalytic system is characterized by sufficient bandgap, stability, adequate morphology, high surface area, and reusability [34]. There are two types of photocatalytic reactions, i.e., homogeneous and heterogeneous photocatalytic reactions. The photocatalytic reagents are largely used to degrade or mineralize hazardous materials into CO2 and H2O, deactivation and destruction of microorganisms, decomposition of air pollutants, and degradation of waste plastics. The metal oxide nanoparticles and their composite materials are well known for their photocatalytic behavior in the presence of UV radiation [35,36]. The photocatalysis on the surface of metal oxide nanoparticles is mediated by valence and conduction bands. The valence and conduction bands are regarded as holes and electrons. Electrons are shifted from valence to conduction band through a proper bandgap in the presence of UV light (Figure 2). The transfer of electrons results in oxidation and reduction. Ultimately this process is leading the formation of reactive oxygen species (ROS). ROS is usually responsible for the degradation of dyes (Scheme 1) [36-43]. Finally, photocatalysis is related to oxidation and reduction processes on the surface of any metal oxide and its composite material. The process is mediated by valence bands (VB) such as holes (h+) and conduction bands (CB) such as electrons (e-) which are generated by the absorption of ultra-violet light. The photo-generated pairs of h+ and e- accelerate the formation of highly aggressive species, i.e., hydroxyl (OH−) or superoxide radicals from the moisture and atmospheric oxygen. Such species are sufficient to oxidize and decompose organic materials or smell gas and destroy bacteria [37].

Figure 2. Shifting of electrons from valence to conductance band.
Scheme 1. Schematic representation of photodegradation of organic dyes.

Photocatalysis is an efficient process for the degradation of organic substances, microbial disinfection, and mineralization of hazardous compounds due to the formation of OH⁻ ions (strong oxidizing agent). If the reaction occurs in the presence of oxygen and water, the electron in the conduction band is picked up by oxygen and gives rise to a superoxide radical anion; water is oxidized into OH radical on the oxidation site. The formation of these two reactive species results in the complete mineralization of organic pollutants and reactions e⁻/h⁺ pair with different electron donors and acceptors. Further, the redox potentials of valence and conduction band are sufficiently positive and negative for the generation of OH⁻ and superoxide radicals [16, 44, 45].

3. Metal Oxide Nanoparticles as Photocatalysts

The transition metals and their oxides have been used in different catalytic activities. They show many special properties and industrial applications. They can also behave as superconducting materials, ceramics, crystalline lasers, photoactive materials, photosensitizers, sensors, etc. Metal oxides have played a significant role in the areas of physical, chemical and materials sciences. The metal oxides can easily be synthesized and are multifunctional [46]. Metal oxides have also been potentially utilized in environmental remediation, energy production, storage, and conversion. They exhibit advanced and different functional properties due to crystalline structure, morphology, doping, intrinsic defects, and composition [47-49].
In general, when metal oxide nanoparticles having wide-bandgap are irradiated with light energy, the positive hole-electron pairs are formed; substrates may adsorb on the surface of photocatalyst and react directly or indirectly with the generated holes and electrons [50]. Metal oxide nanoparticles (Figure 3) have been reported to degrade the organic pollutants and toxic inorganic substrates into readily degradable compounds even mineralize them into less harmful carbon dioxide and water [51]. The reported metal oxide nanoparticles (MO NPs) were utilized in the degradation of different dyes given as below:

3.1. ZnO Nanoparticles (ZnO NPs).

Zinc oxide (ZnO) is a white powder and commonly used in ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, plastics, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, and fire retardants. ZnO nanoparticles (ZnO NPs) are potentially used in cosmetics, textiles, microelectronics, catalysts, semiconductors, antimicrobial agents, photocatalysis, and environmental remediation. Due to stability, direct wide gap, and large binding energy at normal temperature, ZnO NPs are used as photocatalysis, solar cells, and light-emitting diode [52,53]. Tayeb and others [54] studied the applications of ZnO NPs in the photodegradation of methylene blue from the aqueous solution. After UV irradiation time of 90 min, 97% methylene blue was degraded in the presence of ZnO NPs. The photocatalytic activity of ZnO NPs was reported by Bibi et al. [55] under UV irradiation to degrade Remazol brilliant blue. Maximum dye degradation was found as 85.91 % at irradiation time 60 min. Rodrigues and other workers [56] studied the applicability of ZnO NPs in the photocatalytic degradation of RB 19 and RB 21 dyes under UV light and found the efficiency of photodegradation as 100 % and 91 % after 6 hrs for RB 19 and RB. They observed that the photocatalytic activity was highly affected by dye concentration, length to diameter ratio of photoreactor, and catalyst size. Maureen and others [57] reported using ZnO NPs to degrade malachite green dye under UV light. The maximum percentage photodegradation of dye has
been achieved as 96.31% at dosage 0.5 g and irradiation time 150 min. They studied the kinetics of degradation and found the suitability of the pseudo-first-order kinetic model.

3.2. Titanium dioxide nanoparticles (TiO₂ NPs).

Titanium dioxide nanoparticles (TiO₂ NPs) have been synthesized for different applications such as photocatalysis, solar cell, antibacterial agents, and wastewater treatments. These are easily available, low toxic, and cost-effective [58,59]. TiO₂ NPs are very effective photocatalysts due to their unique electronic and optical properties, chemical stability, and sufficient bandgap and are capable of degrading the inorganic and organic pollutants [60-62]. Gautam and others [63] investigated the effect of anatase and rutile TiO₂ NPs on the degradation of methylene blue under short ultra-violet irradiation. The maximum percentage degradation of anatase and rutile TiO₂ NPs were obtained as 88% and 77% for methylene blue. Kaur et al. [64] studied the potential use of green synthesized TiO₂ NPs (using Carica papaya leaves extract) to degrade RO-4 dye under ultra-violet radiation. The percentage of dye degradation was found at 91.19% within 180 min. Khade and other co-workers [65] showed that the anatase TiO₂ NPs were capable of degrading the methyl orange from an aqueous solution under ultra-violet radiation. More than 93% dye was degraded within 150 min. Nabi et al. [66] used the green synthesized (using Lemon extract) TiO₂ NPs to degrade Rhodamine B under UV-Visible radiation. The experimental results showed that the TiO₂ NPs were highly capable of degrading Rhodamine B from the aqueous solution.

3.3. Zirconium oxide nanoparticles (ZrO₂ NPs).

Zirconia nanoparticles (ZrO₂ NPs) show many advanced properties, i.e., excellent color, good strength, high chemical stability, corrosion resistance, and microbial and chemical resistance. ZrO₂ NPs exist in cubic, tetragonal, and monoclinic phases under normal pressure and different temperatures. The monoclinic ZrO₂ phase is stable up to 1100°C, the tetragonal ZrO₂ phase exists in the temperature range of 1100 – 2370°C, and the cubic phase is found at higher temperature (above 2370°C) [67-69]. Mansouri et al. [70] studied the use of ZrO₂ NPs to degrade methyl orange under ultra-violet light and observed more than 97% dye degradation during 80 min. Basahel and others [71] reported the use of monoclinic ZrO₂ NPs in the removal of methyl orange from aqueous solution in the presence of ultra-violet radiation; more than 95% dye was degraded within 110 min. Saeed et al. [72] studied the palladium and platinum-supported ZrO₂ NPs in the photodegradation of indigo disulfonate; they observed the percentage degradation as 96% and 94% for indigo disulfonate in the presence of Pd and Pt supported ZrO₂ NPs within 14 h.

3.4. Iron oxide nanoparticles.

The iron oxide nanoparticles (IONPs) show many unique properties such as larger surface area, super-paramagnetism, high surface to volume, and easily separable. IONPs have been widely used in agriculture, environmental remediation, and biomedicines. The most common IONPs are magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and hematite (α-Fe₂O₃) nanoparticles [73]. Parhizkar and Habibi [74] studied the use of α-Fe₂O₃ nanoparticles in the photocatalytic degradation of reactive red 4 (RR4) dye under ultra-violet light. The experimental results showed that 52% of dye degradation was found in 135 min. Długosz et al. [75] reported the enhanced photocatalytic activity of ZnO NPs after incorporation with Fe₃O₄.
nanoparticles. The maximum percentage photodegradation of this material was found at 95.61% for trypan blue and 63.02% for methylene blue. Alagiri and Hamid [76] considered the potential application of α-Fe₂O₃ nanoparticles in the degradation of methylene blue under UV radiation. The results showed that more than 90% degradation of methylene blue was recorded in the presence of UV radiation and α-Fe₂O₃ nanoparticles. Rincon Joya and others [77] used the α-Fe₂O₃ nanoparticles to degrade Rhodamine B and atrazine under ultra-violet radiations. Within 40 min, the percentage degradation of 59% for atrazine and 40% for Rhodamine B were achieved.

3.5. Cerium oxide nanoparticles (CeO₂ NPs).

Cerium dioxide (CeO₂) or ceria is the most stable oxide of cerium and the second reactive member of the lanthanide series. The +4 oxidation state of cerium in CeO₂ is responsible for its higher stability. CeO₂ nanoparticles (CeO₂ NPs) are basically used in biomedicine, drug delivery, bio scaffolding, environment, and different biological activities [78]. Pouretedal and Kadkhodaie [79] studied the applicability of CeO₂ nanoparticles in the degradation of methylene blue from the aqueous system under UV-Visible irradiation. The highest degradation was obtained with 1.0 g/L CeO₂ at pH 11 within 125 min. Majumder and other workers [80] reported the complete degradation of methylene blue from textile effluents using CeO₂ NPs under UV-Visible radiation within 175 minutes. Ravishankar et al. [81] studied the photodegradation of trypan blue in the presence of UV light and CeO₂ NPs. About 100% dye degradation was observed within 135 minutes from the aqueous system.

3.6. Manganese dioxide nanoparticles (MnO₂ NPs).

Manganese dioxide (MnO₂) is also known as pyrolusite and is used in ceramic industries, glassmaking, batteries, etc. MnO₂ nanoparticles (MnO₂ NPs) generally possess a unique 2D structure used in biomedicine, fluorescence sensing, magnetic resonance imaging, and cargo-loading functionality [82]. Rahmat et al. [83] used the MnO₂ NPs to degrade crystal violet from wastewater under visible light. After 90 min, the percentage degradation of the dye was achieved as 97%. Khan and others [84] used the activated carbon incorporated with MnO₂ NPs for the photodegradation of Congo red (CR) dye from aqueous solutions. This material was capable of degrading 98.53% of Congo red dye within 5 min. Chan et al. [85] were reported the utilization of MnO₂ NPs in the degradation of Rhodamine B from aqueous effluent under visible light. The percentage degradation of 90.3% was found at an irradiation time of 120 min. Hamza [86] utilized the MnO₂ NPs in the photochemical removal of alizarin red (AR) dye from wastewater using ultra-violet light and found the maximum percentage degradation of 80%.

3.7. Cupric oxide nanoparticles (CuO NPs).

Copper (II) oxide nanoparticles (CuO NPs) are brownish-black colored with a narrow bandgap and generally monoclinic structure. They have interesting properties such as good thermal conductivity, high stability, good selectivity, photo-voltaic properties, and antimicrobial activities. CuO NPs can also be used in ceramics, magnetic storage media, gas sensors, and high-tech superconductors [87-92]. Singh et al. [93] utilized the green synthesized CuO NPs (using Psidium guajava leaves extract) for the photodegradation of Nile blue and yellow 60 in an aqueous solution. Within 120 min, 93% of Nile blue and 81% of yellow 60 were degraded. Sharma and Dutta [94] reported the highly stable CuO NPs with valence band
edge (2.59 eV) and conduction band edge (0.29 eV) and used such nanoparticles in the degradation of acid orange-74 dye under ultra-violet radiations. They found the CuO NPs had excellent photocatalytic dye degradation ability. Narasaiah et al. [95] have synthesized the CuO NPs using the leaves extract of Drypetes sepiaria and found their excellent photocatalytic activity in the degradation of Congo Red. Chauhan and others [96] studied the utilization of CuO NPs in the photodegradation of Victoria Blue (VB) and Direct Red 81 (DR 81) from the aqueous effluent and observed the percentage degradation of more than 96%.

3.8. Tin oxide nanoparticles (SnO\textsubscript{2} NPs).

Tin oxide (SnO\textsubscript{2}) is an n-type semiconductor with a bandgap of 3.6 eV at ordinary temperature. SnO\textsubscript{2} nanoparticles (SnO\textsubscript{2} NPs) show good optical and electrical properties at room temperature, photocatalytic activity, and low resistivity. SnO\textsubscript{2} NPs are also used in the coating, photo-voltaic, photo-sensors, gas sensors, etc. [97-101]. Selvaraj and Roopan [102] reported the utilization of biologically synthesized SnO\textsubscript{2} NPs (using methanolic extract of Cyphomandra betacea) in the photodegradation of methylene blue present in aqueous effluent. The rod-shaped SnO\textsubscript{2} NPs with particle size 21 nm were found excellent photocatalyst to degrade methylene blue in the effluent. Tammina et al. [103] utilized the SnO\textsubscript{2} NPs to degrade methylene blue under the ultra-violet radiations. The smaller-sized SnO\textsubscript{2} NPs exhibited a higher rate of degradation within 30 min. Li et al. [104] considered the photocatalytic applications of SnO\textsubscript{2} NPs in the degradation of methylene blue and Rhodamine B present in the aqueous effluent. More than 90% methylene blue and Rhodamine B were degraded under UV light irradiation within 50 min and 270 min, respectively. Viet et al. [101] used the SnO\textsubscript{2} NPs (synthesized using the hydrothermal method) to degrade methylene blue under sunlight. The smaller-sized SnO\textsubscript{2} NPs degraded 90 % methylene blue within 120 min. Titus and Samuel [105] applied the green synthesized SnO\textsubscript{2} NPs (using methanolic extract of Arachis hypogaea) to degrade Congo red under ultra-violet light; 89 % degradation was recorded after 50 min.

4. Some Common Synthetic Approaches Used in the Synthesis of Metal Oxide Nanoparticles

Based on choice of the medium, the basic synthetic methods used to synthesize metal oxide nanoparticles are generally categorized into liquid phase, biological/green, and vapor state-based methods (Figure 4). The selection of synthetic methods determines many physical and chemical characteristics of metal oxide nanoparticles. These properties include particle size, crystal appearance, and shape of particles, dispersity, and type of intrinsic or extrinsic defects [106-109]. The methods mentioned above are shortly explained as below:

4.1. Liquid phase-based synthetic methods.

4.1.1. Colloidal methods.

The colloidal-based methods are based on the mixing of solutions containing different ions under controlled temperature and pressure. As a result, an insoluble precipitate of nanoparticles is formed and easily separable. These methods are frequently used to synthesize metal, metal oxide, organics, and other nanoparticles [110-112].
4.1.2. Sol-gel methods.

Sol-gel methods are widely used and well-established methods; such methods are used for materials having novel and predefined properties. These methods are based on the interactions between sol (containing solid particles) and the gel (containing solid macromolecule). The major step of this method is the hydrolysis of precursors (especially metal-organic compounds) [113,114].

4.1.3. Sonochemical method.

In such methods, the starting materials are contacted with ultrasonic vibrations for the breaking of chemical bonds. The ultrasonic waves pass through the solution and cause compression and relaxation; it causes acoustic cavitation. Ultimately, thousands to million bubbles undergo collapsing, and a large amount of energy is released into the solution [115-117].

4.1.4. Solvothermal method.

Solvothermal methods have been used to synthesize different nano-based materials, including metal oxide-based materials, by dispersing the precursors into a suitable solvent and then applying moderate temperature and pressure. If the medium is water, then this method is
called a hydrothermal method. This method is dependent on the nature of starting material, composition, ratio, and thermodynamic parameters [10,118].

4.1.5. Microemulsion method.

The microemulsion method consists of two different immiscible phases, which are separated through the surfactant molecules. In this method, a mixture of metallic precursors, oil, water, and surfactants are used and subjected to stirring at ordinary temperature to prepare a homogeneous phase [119,120].

4.1.6. Microwave-assisted method.

The microwave-assisted method is needed very low energy and time; the faster reactions can be performed with high heating rates without any temperature gradient. The mechanism of the synthetic reaction is based on ionic conductivity and polarization. The speed of reactions involving nanomaterials’ preparation favors nucleation and highly dispersed particles [121,122].

4.2. Vapor state synthesis.

4.2.1. Laser ablation method.

The laser ablation technique is generally used to generate nanoparticles through the irradiation of colloidal solutions originating from the bulk materials in water or other solutions. The particles size is dependent on the laser fluence and nature of the liquid medium. This technique is used to synthesize noble stable nanoparticles and does not require stabilizing molecules or chemicals [123,124].

4.2.2. Combustion method.

Combustion methods are highly efficient and energy-saving and can be proceeded in solid, liquid, and gas phases. This method is also called self-propagating high-temperature synthesis and is very common to synthesize metal oxide nanoparticles. Combustion methods initially can take place through the solid, liquid, and gas-phase combustions. The maximum synthesis temperatures are limited by the thermodynamics of the systems [81, 125].

4.2.3. Template synthesis.

The template methods involve the control of crystal growth and nucleation, and the synthetic route is divided into three steps. The first step is the preparation of the template; the second is the applicability of suitable synthetic approaches such as sol-gel, precipitation, hydrothermal, etc. The final step is the removal of the template. The templates may be natural or synthetic; the natural templates include biological molecules, minerals, tissues, etc. The artificial templates include porous materials, nanoparticles, surface-active agents, etc. [126,127].

4.3. Biological or green methods.

The biological or green synthetic approaches used in synthesizing metal oxide nanoparticles have gained much attention due to their efficiency, low cost, and being
environmentally friendly. The main advantages of greener methods are minimizing waste, reducing unnecessary derivatives, simplicity, and no requirement of toxic chemicals. The biological extracts containing different secondary metabolites generally obtained from plants, algae, fungi etc. are used as reducing, capping, or stabilizing agents during the synthesis of different metal and metal oxide nanoparticles [128-131].

Table 1. Some metal oxide nanoparticles synthesized using different synthetic methods.

| Metal oxide nanoparticles | Methods used for synthesis | References |
|----------------------------|-----------------------------|------------|
| TiO$_2$ NPs                | Colloidal                   | [110]      |
| TiO$_2$ NPs                | Colloidal                   | [111]      |
| SnO$_2$ NPs                | Colloidal                   | [112]      |
| ZnO NPs                    | Sol gel                     | [113]      |
| ZnO NPs                    | Sol gel                     | [114]      |
| ZrO$_2$ NPs                | Sonochemical                | [115]      |
| CeO$_2$ NPs                | Sonochemical                | [116]      |
| CeO$_2$ NPs                | Sonochemical                | [117]      |
| Fe$_3$O$_4$ NPs            | Solvothermal                | [118]      |
| Fe$_3$O$_4$ NPs            | Solvothermal                | [10]       |
| MnO$_2$ NPs                | Microemulsion               | [119]      |
| MnO$_2$ NPs                | Microemulsion               | [120]      |
| CuO NPs                    | Microwave-assisted          | [121]      |
| Fe$_2$O$_3$ and Fe$_3$O$_4$ NPs | Microwave-assisted        | [122]      |
| ZrO$_2$ NPs                | Laser ablation              | [123]      |
| ZrO$_2$ NPs                | Laser ablation              | [124]      |
| CeO$_2$ NPs                | Combustion                  | [81]       |
| CeO$_2$ NPs                | Combustion                  | [125]      |
| SnO$_2$ NPs                | Template                    | [126]      |
| TiO$_2$ NPs                | Template                    | [127]      |
| CuO NPs                    | Green                       | [128]      |
| ZnO NPs                    | Green                       | [129]      |
| ZnO NPs                    | Green                       | [130]      |
| TiO$_2$ NPs                | Green                       | [131]      |

5. Nanocomposite Materials of Metal Oxides Used in the Degradation of Organic Dyes

Nanocomposites combine different materials in which at least one of the materials has particle sizes 1-100 nm. Nanocomposite materials have gained a lot of attention due to their improved physical and chemical characteristics. Such materials are suitable for different functional and structural applications in science and technology due to their improved properties, i.e., good mechanical strength, porosity, toughness, electrical and thermal conductivities, dispersibility, and high mobility [132-137]. They have been used to remediation inorganic and organic pollutants, gas sensing, electronic devices, biomedical fields, photocatalytic degradation of organic dyes, etc. The metal oxide-based nanocomposites with advanced surface features, stability, controlled structural and surface features are feasible in the photochemical degradation of organic pollutants. Due to high photodegradation capabilities, controlled bandgap, and efficient synthetic approaches, these materials have been potentially utilized in the photochemical degradation of organic dyes [133-138].
Table 2. Some metal oxide-based nanocomposites are used in the photodegradation of dyes.

| Metal oxide-based nanocomposites          | Dye degraded                             | References |
|-------------------------------------------|------------------------------------------|------------|
| **Graphene oxide/metal oxide**            |                                          |            |
| Graphene oxide/ZnO                        | Rhodamine B                              | [132]      |
| Graphene oxide/TiO₂                       | Rhodamine B and acid green 25            | [133]      |
| Graphene oxide/TiO₂                       | Rhodamine B                              | [134]      |
| Graphene oxide/CuO                        | Methylene blue                           | [135]      |
| Graphene oxide/CuO                        | Methylene blue                           | [136]      |
| Graphene oxide/Fe₃O₄                      | Methylene blue                           | [137]      |
| Graphene oxide/TiO₂ and reduced Graphene oxide/TiO₂ | Eosin Y and methylene dyes | [138]      |
| Graphene oxide/SnO₂                       | Methylene blue                           | [139]      |
| Reduced Graphene oxide/CdO/SnO₂           | Malachite green (MG) and Congo red (CR)  | [140]      |
| Reduced Graphene oxide/TiO₂/CrO₄         | Methylene blue and crystal violet        | [141]      |
| **Polymer/metal oxide**                   |                                          |            |
| Polyaniline/TiO₂                          | Red azo dye (RR45)                       | [142]      |
| Polyaniline/ZnO                          | Malachite green and methylene blue       | [143]      |
| Poly(3,4-ethylenedioxythiophene) (PEDOT)/ZnO | Reactive Red 45 (RR45)                 | [144]      |
| Polystyrene/TiO₂                          | Methyl orange                            | [145]      |
| Polymethyl methacrylate/TiO₂              | Methylene blue                           | [146]      |
| Polymethyl methacrylate/ZnO              | Methylene blue                           | [147]      |
| Poly(3-hexylthiophene)/TiO₂              | Methyl orange                            | [148]      |
| **Metal/metal oxide**                     |                                          |            |
| Ag/ZnO                                    | Congo red                                | [149]      |
| Cu₂TiO₄/CuO                               | Methylene blue                           | [150]      |
| Zn/SnO                                    | Methylene blue                           | [151, 152] |
| Ag/TiO₂                                   | Methylene blue                           | [153]      |
| Co/ZnO                                    | Malachite green                          | [154]      |
| Co/ZnO                                    | Methyl orange                            | [155]      |
| Fe₃O₄/SiO₂                                | Methylene blue                           | [10]       |
| Fe₃O₄/SiO₂                                | Procion Red MX-5B                        | [156]      |
| ZnO/SiO₂                                  | Methylene blue                           | [157]      |
| ZnO/SiO₂                                  | Rhodamine B                              | [158]      |
| TiO₂/SiO₂                                 | Malachite green                          | [159]      |
| SnO/SiO₂                                  | Orange II                                | [160]      |
| SnO/SiO₂                                  | Rhodamine B and Crystal violet           | [161]      |
| ZrO₂/SiO₂                                 | Rhodamine B                              | [162]      |
| ZrO₂/SiO₂                                 | Methylene blue                           | [163]      |
| CuO/ZnO                                   | Congo red                                | [164]      |
| Cu₃O₄-CuO/TiO₂                            | Reactive blue 49 (RB 49)                 | [165]      |
| CuO/TiO₂                                  | Rhodamine B                              | [166]      |
| Cu₃O₄/TiO₂                                | Methylene blue                           | [167]      |
| Fe₃O₄/ZrO₂                                | Methyl red                               | [168]      |
| Fe₃O₄/ZrO₂                                | Methyl orange                            | [169]      |
| **Metal oxide/silica**                    |                                          |            |
| **Metal oxide/metal oxide**               |                                          |            |
| TiO₂/Chitosan–acrylic acid                | Malachite green                          | [170]      |
| Fe₃O₄/Chitosan                            | X-3B dye                                 | [171]      |
| Carbon black-cellulose acetate/ZnO        | Congo red, methyl orange and methylene blue | [172]    |
| MnO₂/cellulose                            | Indigo carmine                           | [173]      |
| ZnO/Cellulose                             | Rhodamine B                              | [174]      |
| ZnO/Cellulose nanofiber                   | Methylene blue                           | [175]      |

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Some metal oxide-based nanocomposites such as Graphene oxide/metal oxide, polymer/metal oxide, metal/metal oxide, metal oxide/silica, metal oxide/metal oxide, and metal oxide/biomaterials were successfully used in the photodegradation of different dyes from aqueous solutions [132-175] (Table 2).

6. Characterisation Techniques for Metal Oxide Nanoparticles and their Composite Materials

Various characterization techniques were used in the exploration of different physical and chemical features of metal oxide nanoparticles and their composite materials. These properties are concerned with surfaces, functionality, behavior, shapes, sizes, arrangement of particles, dispersion, aggregations, elemental composition, etc. The commonly used techniques are Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV-Visible, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Dynamic light scattering (DLS), Zeta-potential, Atomic absorption spectroscopy (AAS), Energy-dispersive X-ray spectroscopy (EDAX), X-ray diffractometry (XRD) and Atomic force microscopy (AFM). Briefly, these analytical techniques can be divided into three categories, i.e., functional property, surface morphology, and other techniques (Table 3) [176-187].

Table 3. Common characterization techniques used to characterize metal oxide nanoparticles and their composite materials.

| Techniques                                      | Applications                                      |
|------------------------------------------------|--------------------------------------------------|
| Analysis for functional properties             |                                                  |
| X-ray diffractometry (XRD)                     | Crystalline and amorphous behavior                |
| Energy dispersive x-ray spectroscopy (EDAX)    | Elemental composition in the nanomaterials        |
| Atomic absorption spectroscopy (AAS)           | Determination of concentrations of different elements in the nanomaterials |
| X-ray photoelectron spectroscopy (XPS)         | Oxidation state                                  |
| UV-Visible spectroscopy                         | Light extinction                                 |
| Fourier transform infrared spectroscopy (FTIR) | Presence of specific functional groups in the nanomaterials |
| Analysis for surface morphology                |                                                  |
| Scanning electron microscopy (SEM)             | Morphological features, surface area, and particle sizes |
| Transmission electron microscopy (TEM)         |                                                  |
| Atomic force microscopy (AFM)                  |                                                  |
| Other analysis                                  |                                                  |
| Dynamic light scattering (DLS)                 | Surface charges and particle sizes               |
| Zeta-potential                                 |                                                  |

7. Conclusions

The present article has discussed the process of photocatalysis and utilization of some efficient metal oxides and their composite-based photocatalyst in the degradation of different dyes from aqueous solutions under suitable irradiations. The used synthetic approaches have also been illustrated in this article. For large-scale operations of wastewater treatment, cost-effective, stable, and eco-friendly metal oxide-based photocatalysts should be designed. The choice of a suitable photocatalyst should be based on their cost, safety, bandgap, high ability to work under sunlight or other visible light, efficiency, and easy recovery and reusability.
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Conflicts of Interest

The authors declare that they have no conflict of interest for the publications of the manuscript.

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