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Metal Oxide Polymer Nanocomposites in Water

Treatments

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Additional information is available at the end of the chapter

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Abstract

Recently, several pollutants such as dyes, pharmaceuticals and phenolic compounds, which can cause toxic effects to human health, have identified in water resources. Water pollution has extensively studied and several conventional techniques, such as chemical treatment, adsorption, biological treatment, and membrane-based separation, have adopted for pollutants removal from wastewater/ water resources. However, these techniques had led to the production of soluble refractory organic compounds and health-threatening bacteria that are hard to be removed. Recently, photocatalysis has considered as one of the most viable technology for water treatment using sunlight to eliminate harmful bacteria and pollutants owing to its cost-effectiveness and high efficiency. Metal oxide and polymers have become promising materials for water treatment owing to their properties, such as surface mobility, large surface area and superb magnetic and optical properties. This book chapter discusses recent design and synthesis of visible light response polymer/metal oxide nanocomposite through several synthetic strategies for water treatment. The results show that the polymer-metal oxide nanocomposite possesses a superior photodegradation activity toward pollutants under simulated visible light. Major challenges in polymer-metal oxide nanocomposite synthesis and future research perspectives for developing alternate synthesis methodologies are also discussed.

Keywords: metal oxides, water treatment, photodegradation, polymer, nanocomposites, pollutants

1. Introduction

Water pollution caused by toxic and hardly-degradable organic and inorganic pollutants posed a severe danger to human well-being and growth. Recently, water pollution has been a significant concern, mostly in areas where people depend on groundwater and surface water for drinking and other domestic purposes [1]. For instance, almost 40% of the world's population has limited access to potable water [2]. The concerns of water shortage have been envisaged to be continued worsen due to the rise in population growth, swiftly improving life standards, rapid modernization, and industrialisation [3]. Shortage of potable water supply is due to the misuse of water resources for irrigation, industry, and domestic purposes in several parts of the world [4]. Industrial wastewaters comprise of several complex organic pollutants such as dyes, oils, detergents, and others, which are known to be carcinogenic to human health and aquatic life [5]. Domestic wastewater containing trace levels of pharmaceuticals, personal care products and others can also induce toxic effects [6]. As a result of the health implication induced by these contaminants, scientists and government authorities are making continuous efforts to address this problem. In the past, the traditional water treatment techniques such as coagulation and adsorption only remove pollutants from water but do not entirely biodegrade them into less toxic compounds [7]. Moreover, water treatment approaches, such as membrane technologies and chemical treatment usually have high operating costs and occasionally produce other poisonous secondary contaminants [8]. Since the water industry is required to produce portable drinking water, there is a need for the development of low-cost and stable approaches to address the day-to-day deterioration of water quality. Among the several approaches used in water treatment, the advanced oxidation processes (AOPs), such as the sonolysis, Fenton reaction, ozonation, and photocatalysis have gained a considerable attention in the removal of pollutants, owing to their simplicity, low cost, high efficiency, easy handling, and good reproducibility [9]. The AOP consist of *in situ* production of nonselective and highly reactive chemical oxidants, such as hydrogen peroxide (H_2O_2), hydroxyl radical (HO^\bullet), superoxide radical ($\text{O}_2^{\bullet-}$), and ozone (O_3) to degrade nonbiodegradable and persistent pollutants into less toxic and biodegradable ones [10]. Recently, photocatalysis has been recognized as one of the most effective approaches for water treatment using sunlight and other light sources as a driving force [11]. More significantly, this technique can degrade several organic pollutants into less toxic molecules and easily biodegradable compounds without forming secondary pollutants. The use of polymer/metal oxide-based photocatalyst materials to decompose pollutants has been recognised as one of the most promising materials [12], owing to their high quantum dimension effect, low cost, photostability, and low toxicity, small-dimension and surface effect [13]. The chapter starts with a brief introduction on a metal oxide, the synthesis approach, fundamentals, and the characterization techniques, followed by a discussion of the current successes made in the development, modification, and applications of the different nanohybrid polymer/metal oxide-based nanocomposites toward the degradation of pollutants in water resources. Finally, the future perspectives and outlooks are also taken into consideration.

2. Inorganic metal oxide

Among the several groups of nanoparticles, inorganic metal oxide has been of considerable interest from both technological and scientific perspective. When metal oxides are transformed into nanometre scale, they show enhanced hybrid properties compared to the pure materials. Metal oxide adopts several structural geometries with an electronic structure, which can be either semiconductor, metallic, or insulator depending on the nature of the structure. The unique features of metal oxides make them the most miscellaneous class of materials, with optical, electronic, electrical, magnetic, catalytic, and photoelectronic properties covering virtually all aspects of solid state physics and materials science, and can find application such as electroceramics, gas sensing, catalysis, superconductors, and energy conversions [14]. However, there are few limitations in using inorganic metal oxides as an absorbent in water treatment. Reducing inorganic metal oxide to nanoscale size may increase the surface area; however, this increment can make the metal oxide unstable and subsequently turn out to be more susceptible to agglomeration owing to the existence of van der Waals interactions [15]. Due to this interaction, the metal oxide may lose their selectivity, mechanical strength, and high capacity. In addition, low quantum yield owing to the rapid recombination of photogenerated charge carriers and the wide energy gap of some metal oxide limits their application in water treatment [16]. To overcome these limitations, metal oxides are immobilized into other supports, such as polymeric materials [17]. Currently, polymeric nanoparticles are used in the elimination of contaminants from water due to large surface area, tunable surface chemistry, perfect mechanical rigidity, and pore size distribution [15].

2.1. Synthesis of inorganic nanomaterials

Currently, the synthesis, characterization, and application of inorganic nanomaterials represent a highly active area of scientific research. Nanofabrication is the design and production of materials with chemical and structural restrictions on the nanometer scale [18]. The design of systematic approaches for the synthesis of inorganic nanomaterials has been a major challenge from both industrial and fundamental viewpoints as the first requirement in any study associated with inorganic nanomaterials involves the synthesis and characterization. An in-depth knowledge and understanding of the synthetic method are crucial in order to design hybrid inorganic nanomaterials with unique properties. The general strategy for preparing inorganic nanomaterials in solution is to separate the nucleation and growth of nanocrystals [19]. The synthesis approaches may be categorized into bottom-up and top-down. The top-down approach uses large homogeneous objects and shrinks them down to the nanoscale, while the bottom-up uses the interactions between the small components, such as colloidal particles or molecules to assemble themselves into more discrete and complex nanoscale structures. The bottom-up approach has been accepted as the most promising technique to address several problems related to the top-down approaches [20]. Both techniques have been used to synthesise nanomaterials. Chemical processes, such as chemical vapor deposition, sol-gel, spray pyrolysis, and template synthesis are employed as bottom-up approaches. The properties and structure of the synthesized nanomaterials can be regulated based on the experimental

conditions employed. The nature of the method used in the synthesizing the nanomaterials allows control over the doping ratio by different elements, particle size, the degree of particle agglomeration, and particle geometry. For example, the liquid-phase approaches, such as sol-gel, coprecipitation, solvothermal/hydrothermal processing, template syntheses and microemulsion have been very resourceful in synthesizing inorganic nanomaterials owing to their capacity to synthesise several ranges of nanomaterials with control morphology and particle size [21]. Those particle parameters give the synthesized inorganic nanomaterials new chemical and physical properties for different applications.

2.2. Inorganic metal oxide polymer nanocomposites

A composite involves an immobilization of two or more materials with distinct chemical and physical properties. Composite materials have a magnificent and several practical applications compared to the individual material due to their extraordinary explicit strength and stiffness, corrosion resistance, low density, high thermal insulation, and toughness [22]. The search for improving the properties of composite materials, which are of lower filler size, led to the design of nanocomposites. Nanocomposites are composite materials with nanoscale morphology such as nanotubes, lamellar nanostructure, or nanoparticles as one of the phases [23]. The properties of nanocomposites are influenced by the individual components, the morphology of the system, volume, and shape fraction of the filler as well as the nature of the interphase between the interface of the components [24]. The enhancement of these properties can be accomplished when there are suitable interaction and good dispersion between the matrix and the nanoparticle. Based on the nature of the matrices, nanocomposites have been classified as a metal, carbon, ceramic, and polymer [25]. Among these nanocomposites, the polymer-based has been recognized as the most attractive in several research areas, such as medicine, optoelectronics, engineering, and water remediation due to their distinctive properties emerging from the individual components [26]. The mixing of polymers and inorganic metal oxide has been an active field of research; in particular, the engineering of flexible nanocomposites has received much attention owing to the significant electrical, thermal, mechanical, and magnetic properties compared to the bulk polymers and the inorganic metal oxide [27]. In this nanocomposites, the polymer material provides convenient processing, structural flexibility, photoconductivity, metallic behavior, tunable electronic properties, and efficient luminescence [28], while the inorganic metal oxide offers high carrier mobility's, band gap tunability, thermal, and mechanical stability as well as dielectric and magnetic properties [29]. In addition to the distinctive features, new or improved phenomena can also occur due to the interface between the polymer and inorganic metal oxide [30]. Due to the large surface area, nanocomposites display many variations in their properties compared to the individual component of the metal oxide. The properties and microstructure of the nanocomposites are influenced by the interfacial interaction between the polymer and the inorganic metal oxide, where a wide range of covalent and hydrogen bonds may prevent phase separation [31].

2.3. Characterization techniques of metal oxide polymer nanocomposites

One of the key features in the design and fabrication of metal oxide/polymer nanocomposites is the in-depth characterization. Characterization of nanocomposites has been mostly centered

on the surface analysis methods and conventional characterization techniques designed to determine the topography of surfaces, composition, morphology, crystallinity, shape, and size. Some of the techniques that have been used in the design and fabrication of nanocomposites have been illustrated [32].

Raman spectroscopy is an analytical technique which depends on inelastic scattering of monochromatic light by molecules due to the molecular excitation, such as rotation, vibration, and translation. Raman spectroscopy determines the vibrational frequencies of molecules that are Raman active and these frequencies rely on the mass and bond strength of atoms.

Fourier transform infra-red (FT-IR) spectroscopy is a significant analytical method which offers appropriate information on the functional groups and structure of a compound. Since FT-IR determines the stretching vibrations of molecules, it can be utilised in the identification of functional groups present in an unknown inorganic and organic compounds.

X-ray diffraction (XRD) is a nondestructive and versatile technique that gives information on the crystal structure, microstructure, chemical composition, lattice constants, and particle size of a material. XRD technique depends on a constructive interference of a beam of X-ray produced in a certain space of direction.

Scanning electron microscopy (SEM) is an electron microscope that scans materials surface with high-energy rays of an electron. SEM makes use of electrons rather than light to scan the surfaces. SEM determined the shape and morphology of material. In addition, morphological properties such as shape, size, and surface features as well as topological data of materials can be obtained.

Transmission electron microscopy (TEM) depends on the beam of electrons generated from an electron gun to interact with the material. TEM determined agglomeration, observation of defects, the effect of annealing, and dispersion in the matrix.

Ultraviolet (UV)-visible spectroscopy is a spectrophotometric technique, which comprises of the measurement of light photons in the UV-visible region. UV-visible spectroscopy measures the intensity of light before and after it has been passed through the material.

Nuclear magnetic resonance (NMR) spectroscopy relied on the population of magnetic nuclei in an external magnetic field to align the nuclei in a finite and predictable number of orientations. NMR gives information on the environment in which the nuclei of atoms are found.

Atomic force microscopy (AFM) is a scanning probe microscopy which uses a small probe to scan across the material to acquire information on the surface of the material. AFM measured the surface of thin films as well as high loading nanoparticles can also be detected.

Photoluminescence (PL) technique is the instantaneous emission of light from the analyzed materials following optical excitation. The effectiveness of PL signals is determined by the properties of the material and the nature of optical excitation. PL is used to obtain information on the compositional analysis of material, band gap, evaluation of several diode materials as well as defect evaluation of light-emitting materials.

Thermogravimetric analysis (TGA) technique is used to measure the weight of a material as a function of material time or temperature at a constant heat rate. TGA is based on heating

a mixture of materials at a high temperature to decompose them in the gas phase. The TGA results are generally obtained as a curve with a percent weight against temperature under controlled atmosphere.

3. Water treatment techniques

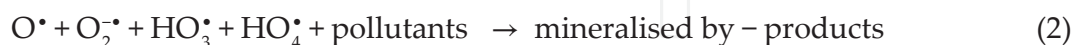
In the past years, several biological, chemical, and physical techniques have been established to eliminate poisonous pollutants from water resources [33]. Despite the availability of several techniques to eliminate pollutants from water, each of these techniques has their intrinsic limitations.

3.1. The use of metal oxide polymer nanocomposite in chemical treatment of wastewater

Chemical treatment is a wastewater treatment technique where chemicals such as hydroxides, carbonates, and sulfides combine with the pollutants in the wastewater to form insoluble precipitates. Chemical treatment is used during wastewater treatment to slow down disinfection. Chemical treatment techniques such as ozonation and oxidation have been used for the removal of contaminants [34].

Oxidation is an essential technique which uses strong oxidising agents to remove pollutants from the wastewater. The two main classes of oxidation technique that have been reported are the chemical and the UV-assisted oxidation that uses hydrogen peroxide, chlorine, potassium permanganate, ozone, and Fenton's reagent [35]. Manganese chloride and magnesium chloride has been used to eliminate Levafix Brilliant Blue EBRA and the results demonstrated a significant increase in the chemical dosage required to remove the dyeing auxiliaries [36]. The discharging solutions of white mud have been used to eradicate Reactive Light Yellow K-6G, Direct Yellow R, Acid Orange II, and Reactive Bright Red K-2BP in wastewater [37]. The results showed almost 90% dye elimination within 90 sec.

Ozonation is also one of the most effective and attractive chemical methods owing to the strong oxidative action of O_3 . In this process, O_3 is decomposed into free radicals follow by instantaneous reaction of the free radicals with the pollutants.



The O_3 is generally created by passing oxygen *via* the gap between two discharging electrodes. During the oxidation process, agents such as high pH, UV, and peroxides are used along with ozone. The optimal pH may be alkaline or acidic based on the nature of pollutants presents in the wastewater. High dose ozonation ($\sim 60 \text{ mgL}^{-1}$) was used for dye removal [38]. They found that the color removal indicates the toxic potential of ozonation by-products.

However, highly toxic and unstable metabolites induce by the oxidation and ozonation technique may cause adverse effects on human health and aquatic life [39]. Chlorination

process, which provides protection against regrowth of pathogens and bacteria, results in undesirable odors and tastes as well as in the formation of disinfection by-products [40]. Although ozonation has shown to be very effective for pollutants removal, sometimes ozonation generate by-products, which are more dangerous than the pollutants itself. In addition, ozonation process has been less attractive due to short lifetime and high operating costs. The combination of processes with polymers and metal oxides aids to cut cost while at the same time achieving effective degradation of pollutants. For example, polyaniline/hexanoic acid/ $\text{TiO}_2/\text{Fe}_3\text{O}_4$ nanocomposite with different ratios of Fe_3O_4 and TiO_2 was fabricated using *in situ* chemical polymerization *via* template-free approach [41]. The nanocomposite with chemical treatment displays a narrow sharp reflection loss peak with strong absorption at a lower frequency owing to the Fe_3O_4 nanoparticles outside the nanorods while the nanocomposite without chemical treatment displays a broad reflection loss peak with weak absorption at a higher frequency.

3.2. Metal oxide polymer nanocomposite in disinfection of biological contaminants

Biological contaminants from pathogens, as well as free-living microbes, such as protozoans, viruses, and bacteria, are possible in water [42]. Biological contaminants are classified as microorganisms, biological toxins, and natural organic matter [42]. The biological treatment techniques for the elimination of pollutants from water are regarded as extremely useful techniques owing to the less chemical usage, low cost, and eco-friendly. The general process of biological treatment techniques involves the transformation of biodegradable wastes into less toxic and simpler forms *via a* biological process using microorganisms such as fungi, bacteria, or algae. The treatment techniques are grouped into the aerobic or anaerobic process. The resultant products after anaerobic treatment are methane, biomass, and carbon dioxide, whereas water, biomass, and carbon dioxide are the resultant products after aerobic treatment. Biological processes such as microbiological, biodegradation, and enzymatic decomposition have also been used for dye removal from wastewaters. The effect of applying irradiation before *Pseudomonas sp.* to Reactive Red 120 dye was studied [43]. Decoloration and mineralization at a lower dose of irradiation were enhanced significantly. Moreover, 90% TOC removal and 98% decoloration were observed after 96 hours of microbial treatment. The potential of *Pseudomonas putida* toward the elimination of Orange II dye was investigated [44]. The results showed 92.8% dye elimination within 96 hours at pH and temperature of 8 and 30°C, respectively.

However, most of these biological treatment techniques are unable to eradicate a wide range of pollutants and most of these pollutants remain soluble in the effluent [45]. Recently, there have been reports on nanomaterials such as Zn, Ag, and Ti as a disinfectant to several waterborne disease-causing microbes owing to their charge capacity. The efficiency of polymer-metal oxide nanocomposites in water disinfections have been emphasized [46]. In particular, a polyaniline/ TiO_2 /graphene nanocomposite was fabricated *via in situ* oxidative polymerization of aniline with TiO_2 and graphene nanoparticles [47]. The as-fabricated nanocomposite demonstrated high antibacterial activity toward *Enterobacter ludwigii* and *Escherichia coli*, indicating its potential as a photocatalyst with antibacterial properties. The enhanced photocatalytic activity

and antibacterial activity was as a result of the low recombination of the graphene electron scavenging property and the sensitising effect of polyaniline. An ultrafiltration membrane of poly(1-vinylpyrrolidone-*co*-acrylonitrile)-*g*-ZnO and poly(ether sulfone)-*g*-ZnO with high antibacterial performances and water flux was synthesized [48]. The results revealed that both membranes possess improved water flux, high antibacterial activities, and antifouling characteristic. The hybrid reverse osmosis membranes with aromatic polyamide thin films and TiO₂ particles was prepared through a self-assembly route [49]. The nanocomposite under irradiated UV light showed enhanced photocatalytic bactericidal efficiency compared to those under darkness and light condition. The nonskinned anatase/poly(vinylidene fluoride) microporous membrane was synthesized without any loss in anatase using the dry cast method [50]. The as-synthesized nanocomposite membrane showed a strong bactericide effect compared to the membrane with only UV light.

3.3. Metal oxide polymer nanocomposite in adsorptive technologies

Water can be purified in several ways, such as filtration, desalination, adsorption, osmosis, sedimentation, and disinfection [4], however, adsorption holds several benefits over the other techniques [51]. Adsorption is a surface occurrence where adsorbate are concentrated on the adsorbent surface and the process can be chemisorption or physisorption base on how the adsorbate get adsorb onto the surface of the adsorbent [52]. In this process, pollutants may adsorb on the adsorbent surface via various forces such as electrostatic, hydrogen bonding, and van der Wall interaction [53]. Normally, the adsorbents possess porous structures to permit fluid to pass through faster and increase the surface area. The adsorption process is an economical and simple technique for pollutants elimination from water since it does not require additional chemicals, large amounts of water and high amounts of energy [54]. In developing countries where there is a limited access to huge amounts of financial resources and power, this cheap and simple method might be a feasible alternative. The mechanistic process of adsorption permits flexibility in the development and usage of adsorbent. An isotherm is used to identify and describe the mechanism of adsorption between the adsorbate and adsorbent [55]. There are several adsorption isotherms, but the most commonly used isotherms are Langmuir and Freundlich. Adsorption relies on several factors such as temperature, contact time, pH, particle size, concentration of pollutants as well as the nature of the adsorbent, and adsorbate [56]. The elimination of pollutants from wastewater and water through adsorption are normally carried out using activated carbon, low-cost adsorbents, nanoparticulate adsorbents, and others. As a result of the large specific surface area, nanoadsorbent shows an extensively higher rate of adsorption for pollutants compared to the powdered activated carbon [57]. Recently, several inorganic and organic adsorbents, such as activated carbon, zeolites, clay minerals, biosorbents, montmorillonite, polymer-based adsorbent, trivalent, and tetravalent metal phosphates have been employed as an adsorbent in the adsorption process [58]. Among them, polymer/metal oxide nanocomposite containing polymers, such as polypyrrole, polythiophene, polyfuran, and polyethyleneimine have a strong affinity toward cations owing to the electrostatic interaction between the positively charged ions of the metal oxide and the lone pair of the polymers [59]. In addition, the presence of positively charged nitrogen atoms in polypyrrole offers a potential application in adsorption process as adsorbent [60]. A polyaniline-modified TiO₂ nanocomposite

was synthesized through the *in situ* chemical polymerization of aniline in TiO_2 solution [61]. The as-synthesized nanocomposite showed an excellent regeneration and adsorption performances with maximum adsorption capacity (454.55 mg/g) with adsorption equilibrium time of 5 min. The acetate/polypyrrole/ TiO_2 , succinic-polypyrrole/ TiO_2 , tartaric/polypyrrole/ TiO_2 and citric/polypyrrole/ TiO_2 composites were fabricated [62] and the results indicate that the hydroxyl group significantly influenced the adsorption capacity and the surface physicochemical properties of the nanocomposite. Moreover, tartaric/polypyrrole/ TiO_2 , tartaric/polypyrrole/ TiO_2 and citric/tartaric/ TiO_2 showed an improved adsorption capacity of 3–4 times toward ARG and MB compared to that of acetate/polypyrrole/ TiO_2 and succinic/polypyrrole/ TiO_2 . In addition, all the nanocomposites displayed an excellent adsorption capacity within 30 min and can be reused without any reduction in capacity for at least 4 times. The hybrid ternary reduced graphene oxide(rGO)/ ZnFe_2O_4 /polyaniline nanocomposite was fabricated through the *in situ* polymerization of aniline on the ZnFe_2O_4 and rGO surface [63]. The as prepared composite exhibited a superior adsorption performance in the sewage purification process. Moreover, the thermodynamic data confirmed that the adsorption behavior of the nanocomposites conforms to the Langmuir isotherm with a second-order kinetic model.

3.4. Application of metal oxide polymer nanocomposite in membrane technologies

Currently, membrane technologies have been more efficient in water and wastewater treatment owing to their effective removal of pollutants without producing any harmful by-products. Generally, the basic principle of membrane technology is to apply semipermeable membranes to eliminate particles, gases, fluids, and solutes. For the effective separation of pollutants from water reservoirs, the membrane must be water permeable as well as less permeable to particles or solutes. Water treatment by membrane technologies can be the effective removal of pollutants due to their feasibility, environmentally friendly and cost-effective [64]. Even though inorganic membranes are gaining more consideration, the majority of membranes are made of polymeric materials. Polymer materials such as polysulfone, cellulose nitrates and acetate, polytetrafluoroethylene, polypropylene, polyethersulfone, polyacrylonitrile, polyimide, polyvinylidene fluoride and polyvinyl alcohol are the most extensively used organic membrane materials. These materials are well-known as alternative approaches to pollutants removal owing to their mechanical stability, excellent permeability, chemical resistance, and selectivity of permeate [65]. The immobilization of metal oxide nanoparticles in polymer membrane has been effective for the photodegradation of contaminants in water treatment [66]. For example, membranes containing nano- TiO_2 effectively degrade contaminants (mostly chlorinated compounds) in the water system [67]. The use of TiO_2 immobilized on polyethene membranes has also proved to be very effective in degrading 1,2-dichlorobenzene [68]. A complete degradation of 4-nitrophenol was observed when a nanocomposite membrane consisted of polymers and alumina *via* layer-by-layer adsorption of citrate stabilised Au nanoparticles and polyelectrolytes [69]. A nanocomposite membrane coated with CoFe_2O_4 -(rGO) and polyvinylidene fluoride (PVDF) on a carbon fiber cloth was fabricated in a PVDF casting solution [70]. The as-fabricated nanocomposite functioned as the cathode membrane to efficiently decompose the contaminants in the water system compared to the microbial fuel cell membrane bioreactor system. The commercial TiO_2 nanoparticles modified with polyaniline was synthesized using the *in situ*

polymerization to enhance the property of membrane antifouling and avoid particle agglomeration [71]. The as-prepared nanocomposite membranes showed higher porosity, fewer microvoids, larger surface and finger-like pore size compared to the control polysulfone membrane. In addition, the results revealed that 1.0 wt% of the nanocomposite membrane exhibited water permeability, excellent hydrophilicity, and antifouling property with high rejection rate. The polysulfone ultrafiltration membranes with polyethylene Glycol 1000 as additives and polyaniline/titania nanocomposites were synthesized through the phase inversion technique [72]. The as-synthesized composites membranes displayed enhanced permeability, improved porosity, better hydrophilicity, excellent antifouling ability, and water uptake compared to the polysulfone membranes. Through the phase-inversion route, self-synthesized Cu_2O nanoparticle was introduced into the poly(ether sulfone) mixed-matrix membrane [73]. About 1.5 wt% of the nanocomposite showed an improved water permeability of $66.72 \times 10^{-9} \text{ m s/k/Pa}$. Poly(l-lactide)/ TiO_2 nanocomposite membrane was prepared by immersion precipitation method [74]. Moreover, the porosity and pore size on the nanocomposite membrane surface become denser with increasing the TiO_2 loading. The as-prepared nanocomposite membranes displayed enhance recycling and antifouling activity compared to the bulk poly(l-lactide) membrane. The hybrid polyacrylic acid/ TiO_2 ultrafiltration membranes with enhanced antifouling performance were fabricated by incorporating TiO_2 particles grafted with polyacrylic acid [75]. The results showed that the nanocomposite membrane exhibited improved hydrophilicity, dispersed well in the membrane medium, excellent antifouling performance, and water flux compared to the pure polyacrylic acid membranes. A polyvinylidene fluoride ultrafiltration membrane was improved through the phase inversion route by incorporating TiO_2 particles in a polyvinylidene fluoride solution [76]. The results showed that the nanocomposite membranes display a larger and longer macrovoid which resulted in an enhanced water flux activity due to the increased surface hydrophilicity. A hybrid SiO_2 /polyvinylchloride membrane with different loading of SiO_2 nanoparticles was prepared using the phase-inversion technique [77]. The membrane nanocomposite with 1.5 wt% SiO_2 nanoparticles displayed better performance toward bacterial attachment and protein absorption, higher flux recovery ratio, and better antifouling performance compared to the bare polyvinylchloride membrane. Hence, membrane nanocomposites exhibited applicable potential in water and wastewater treatment due to their excellent antifouling performance, cost-effectiveness, and better elimination efficacies of total bacteria (>93.6%), chemical oxygen demand (>82.9%), and suspended solids (>97.2%). The nanoporous poly(ether sulfone)/ TiO_2 ultrafiltration membranes were fabricated through a nonsolvent-induced phase separation route [78]. The modified poly(ether sulfone) membrane revealed increased wettability, reduced pore size, and surface-free energy. In addition, the modified membrane with 0.5 wt% TiO_2 nanoparticle loading demonstrated enhanced antifouling activity with ~80% water flux recovery compared to the control membrane.

3.5. Metal oxide polymer nanocomposite in ion exchange technologies

Hard water often leaves a grey residue when used in cleaning and washing. An ion exchange technique which is similar to the reverse osmosis technique can be used to soften the water. Ion exchange technique is a water treatment technique, which successfully eliminates pollutants from aqueous solutions *via* a strong interaction between the functional group on the charged

contaminants and the ion exchange resins [79]. Thus, this technique comprises of exchange of ions to form strong bond between the resins and solutes to achieve efficient separation. Generally, ion exchange membrane is categorized into cation and anion exchangers based on the form of ionic group attached to the membrane medium. The most common used anion exchange are weak base-type, which are type I ion exchange resins ($-\text{N}(\text{CH}_3)_3$), and type II ion exchange resins ($-\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$), while cation exchangers are the weak acidic carboxylate groups ($-\text{COO}-$) and strong acid-type groups ($-\text{SO}_3$) [80]. The modification of commercially existing ion exchangers and the design of appropriate organic polymeric and inorganic metal oxide membranes with biocide and catalytic performance have been of great interest [81]. Beside polymeric membranes, ion exchange membranes can also be fabricated from other materials such as phosphate salts, bentonite, and zeolites [27]. However, these membranes are ineffective compared to the polymeric membranes owing to their high cost, too large pores and relative bad electrochemical properties [82]. In addition, ion exchange membranes fabricated from polymeric materials exhibits excellent conductivity and high chemical stability [83]. Thus, the combination of polymer materials with inorganic metal oxides offer a new form of ion exchangers with high stability, excellent reproducibility, high ion exchange capacity, and mechanical stability as well as good selectivity toward metal ions [84, 85]. Recently, several excellent metal oxide/polymer ion exchange membranes have been fabricated and effectively used in water remediation process. For instance, nanocomposite material formed by the immobilization of multivalent metal acid salts into conducting polymers, such as polypyrrole, polyaniline, or polythiophene, offers a hybrid ion exchange membrane with high reproducibility, stability, granulometric, and mechanical properties as well as excellent selectivity for heavy metals and ion-exchange capacity [86]. These results indicated that the hybrid organic-inorganic ion exchangers were highly selective toward Cd(II). A hybrid polypyrrole polyantimonic acid nanocomposite with good reproducibility, selectivity toward certain heavy metals, excellent ion-exchange capacity, thermal, and chemical stability was fabricated by mixing hydrated antimony oxide with polypyrrole [83]. The as-fabricated nanocomposite was extremely selective toward Hg(II). A crystalline acrylamide stannic silicomolybdate nanocomposite ion exchanger was prepared at pH 0.63 [87]. The authors revealed that the nanocomposite demonstrated a superior exchange capacity of 1.64 meq/g compared to the pure stannic silicomolybdate (0.40 meq/g). Based on the distribution studies results, several significant binary separations such as Cd(II)-Pb(II), Cd(II)-Cu(II), Al(III)-Pb(II), Al(III)-Cu(II), Zn(II)-Pb(II), and Zn(II)-Cu(II) were observed on the acrylamide stannic silicomolybdate column. A hybrid poly-*o*-toluidine/ $\text{Ce}_3(\text{PO}_4)_4$ and poly-*o*-toluidine/ $\text{Sn}(\text{WO}_4)_2$ nanocomposite with high stability, good reproducibility, high ion exchangeability, and good selectivity for heavy metals was fabricated by incorporating orthotoluidine (poly-*o*-toluidine) into $\text{Ce}_3(\text{PO}_4)_4$ precipitate [88, 89]. The distribution studies demonstrated that the nanocomposites were extremely selective toward Cd(II). Using a fibrous-type polypyrrole/ $\text{Th}_3(\text{PO}_4)_4$ cation-exchanger nanocomposite, the separation of Pb(II) from aqueous solution was explored [90]. The nanocomposite was fabricated by immobilizing polypyrrole into $\text{Th}_3(\text{PO}_4)_4$ precipitate. Based on the distribution studies, the nanocomposite exhibited excellent selectivity for Pb(II) on the $\text{Th}_3(\text{PO}_4)_4$ column. A hybrid poly(methyl methacrylate)/ $\text{Zr}_3(\text{PO}_4)_4$ cation-exchanger nanocomposites were synthesized by immobilizing poly(methyl methacrylate) into $\text{Zr}_3(\text{PO}_4)_4$ precipitate [91]. Based on the sorption studies, the nanocomposite was highly selective to Pb(II). A novel cellulose

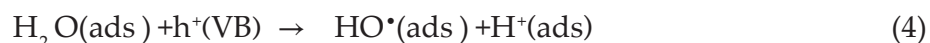
acetate/Zr(IV) molybdophosphate (ZMP) cation exchanger was fabricated by incorporating organic polymers into multivalent metal acid salts [92]. The as-fabricated nanocomposites displayed a superior selectivity toward Cr(III) on the ZMP column. A novel polymeric-inorganic cation-exchanger nanocomposite was fabricated through a sol-gel route by immobilizing polyaniline into zirconium titanium phosphate [93]. The nanocomposite showed high ion-exchange capacity (4.52 meq/g), good thermal and chemical stability compared to the bulk polyaniline and zirconium titanium phosphate. Moreover, the distribution studies of the nanocomposite revealed highly selectivity to Pb(II) and Hg(II).

3.6. Metal oxide polymer nanocomposite in photocatalytic degradation of pollutants

Recently, personal care and pharmaceutical products used in drugs, cosmetics, agricultural practice, and veterinary medicine have been considered as emerging contaminants [94]. Moreover, organic dyes normally used in printing, photographic, and textile industries are often wasted during the dying process and discharge into the wastewater effluents. The existence of even low concentrations of pollutants in the wastewater streams extremely affects the nature of water, which makes hard to be oxidised or biodegraded. The photodegradation of pollutants in wastewater and water systems using photocatalysis process has been an effective approach compared to the conventional approaches without high energy consumption as well as the formation of highly toxic and poor biodegradable products [95]. Photocatalysis is an AOP employed in wastewater and water treatment process, such as degradation of highly toxic pollutants as well as the oxidative elimination of microbial pathogens and micropollutants [96]. Photocatalysis process uses semiconductors such as metal oxides, nitrides, and sulfides. Normally, a metal oxide is photoactivated by the incoming photon from the light source. As a renewable and safe energy source as well as abundant and clean, natural sunlight has been the ideal source of energy for the activation process [97]. The sun distributes almost four orders of magnitude of its energy to the earth surface annually larger than the energy consumed by humans. When the metal oxide is irradiated by sunlight, electrons and holes are generated according to Eq. (3) only if the energy of the incident photons is equal to or greater than (\geq) the metal oxide band gap energy (**Figure 1**).



The photocatalytic reaction is initiated when photogenerated electrons are transferred from the filled valence band (VB) of the metal oxide to the empty conduction band (CB), leaving positive holes in the VB (h_{VB}^+). The photogenerated electron then migrates to the metal oxide surface where separation and redox reaction occur. Both reduction and oxidation processes can occur on the surface of the photoexcited metal oxide only if the process is thermodynamically feasible. The photoinduced holes at the VB then react with the adsorbed water molecules to produce OH^\bullet radical (Eq. (4)).



Instantaneously, electrons in the CB (e_{CB}^-) also react with the adsorbed oxygen molecule to produce $\text{O}_2^{\bullet-}$ radical as shown in Eq. (5).



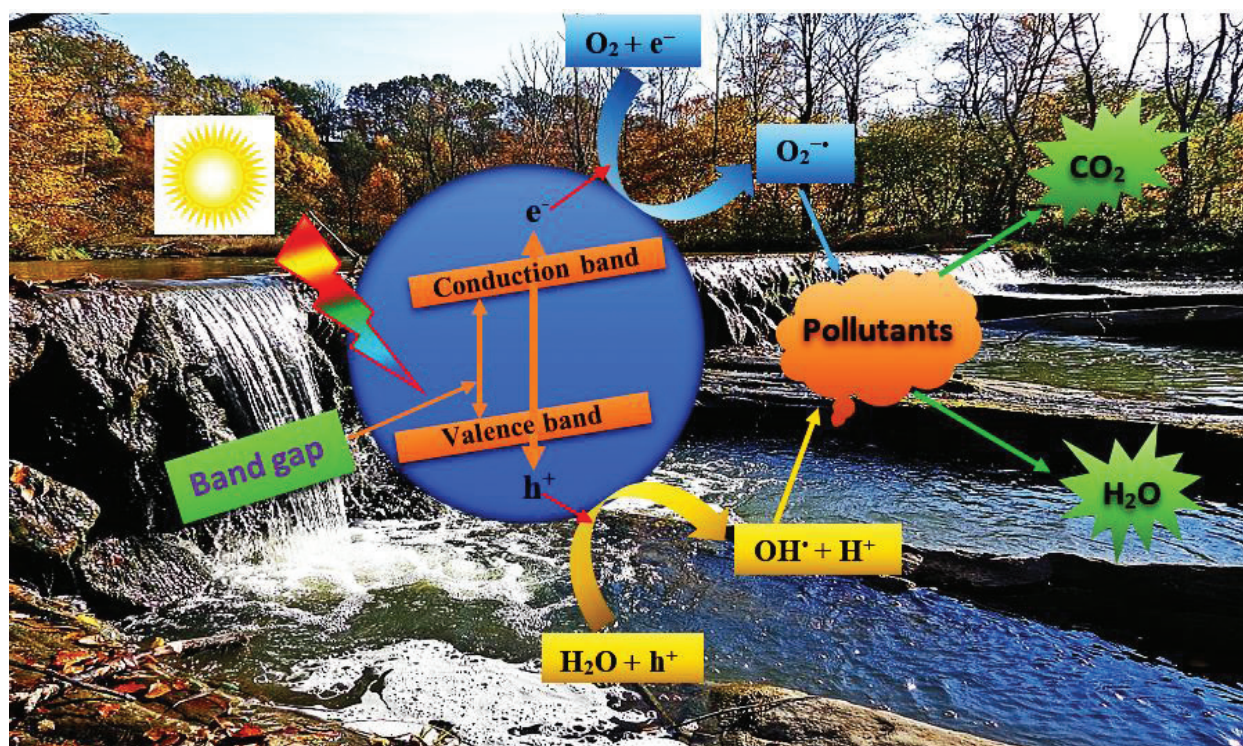
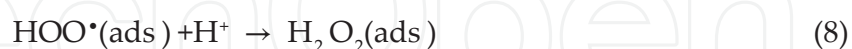


Figure 1. Schematic of photocatalysis process toward the photodegradation of pollutants.

The HO^\bullet and $\text{O}_2^{\bullet-}$ radicals formed are extremely powerful oxidizing and reducing agent to attack the adsorbed pollutants (Eq. (6)), causing them to mineralize depending on their stability level and structure.



Sometimes, the $\text{O}_2^{\bullet-}$ radical may not take part in further oxidation process and gets protonated to generate a hydroperoxyl radicals (HO_2^\bullet) and subsequently into H_2O_2 , which further decomposes into extremely reactive HO^\bullet radicals (see Eqs. (7)–(9)).



Due to the ability of some of the metal oxides to easily absorb some of the visible light, another mechanism of photodegradation of pollutants was considered. This mechanism consist of the pollutants excitation under simulated visible light irradiation from the ground state (pollutant) to the triplet excited state (pollutant*) [98]. As a result of the migration of electron into the CB of the metal oxide, these excited state pollutants species are transformed into a semioxidized cation radical (pollutants⁺). The trapped electrons combine with the dissolved oxygen molecules to generate $\text{O}_2^{\bullet-}$ radical anions, which can further undergo a series of reactions to generate an HO^\bullet radicals which can then oxidize the adsorbed pollutants.

Since the report by Fujishima [99], numerous metal oxide-based photocatalysts has attracted substantial consideration in the degradation of highly toxic and nonbiodegradable compounds

[100] owing to its exceptional optical properties, nontoxicity, low cost, and high stability toward photo and chemical corrosion [101]. However, the major limitation of some of the metal oxide-based photocatalyst materials for potential applications includes the fast recombination of the charge carriers due to the low quantum yield and wide band gap limitation in harvesting a wider portion of the solar energy [102]. Hence, the design of metal oxide-based photocatalyst materials for the degradation of contaminants, which are of high photostability, visible light active, and photoactivity are of considerable interest to provide a fundamental insight into the underlying mechanism of photocatalysis as well as designing a more efficient and easily tunable metal oxide-based photocatalyst materials. To address these restrictions, metal oxides are normally immobilized with polymers. The incorporation of metal oxide into a polymeric material with appropriate energy levels enhances the charge migration between the inorganic metal oxide and polymer to reduce the recombination of the charge carriers [103]. Recently, nanocomposites of several conductive polymers and metal oxide nanoparticles have been fabricated with improved photocatalytic responses in the visible region. Polymeric materials are currently been applied in water treatment due to their pore size distribution, perfect mechanical rigidity, tunable, and large surface area [104]. For example, some organic nanofiber membranes, such as cellulose, polyacrylonitrile, polyvinylpyrrolidone, polytetrafluoroethylene, and polyvinyl acetate are considered as an excellent catalyst supports owing to their high porosity, high permeability, large surface area and good flexibility [105]. The improvements in the fabrication approach employed for designing materials, the characterization and computational techniques have facilitated the fine-tuning of compositional and structural characteristics of materials. The novel porous polytetrafluoroethylene nanofiber membrane with Fe_2O_3 was prepared through a three-step method [105]. Under simulated UV light irradiation, the porous nanocomposite displayed superior photocatalytic degradation toward Acid Red dye with a degradation efficiency of >99% after 80 min. TiO_2 /polypropylene nanocomposite has been reported to show superb photocatalytic performance toward pollutants degradation [106]. The photocatalytic performance of a transition metal coordination polymer(TMCP)/polyoxometalate nanocomposite was enhanced by immobilizing polypyrrole into the TMCP surface *via* a superficial *in situ* chemical oxidation polymerization method [107]. Under simulated visible light irradiation, the as-prepared nanocomposite displayed better photocatalytic performance toward the degradation of Rhodamine B (RhB) dye. Transition metal ions were incorporated into TiO_2 /fly-ash cenospheres with poly(o-phenylenediamine) through ion imprinting technology [108]. The results demonstrated that the as-prepared nanocomposite effectively photodegrades the tetracycline with a photodegradation rate of 71.7%. A silica nanohybrid with different Ru(II)-polypyridyl nanocomposites exhibited improved photocatalytic degradation with respect to Rhodamine 6G dye compared to the functionalized silica nanohybrid [109]. Hydrothermal and electrospinning route was used to prepare polyvinylidene fluoride/titanium dioxide nanocomposite with different compositions of anatase, brookite, and rutile and the nanocomposite displayed a relatively high photocatalytic degradation toward phenol [110]. The two types of polysulfone/carbon-covered alumina/ TiO_2 membranes were successfully prepared and their activity toward RhB dye under visible light irradiation was tested [111]. The results displayed that the nanocomposite without a fabric membrane degraded 78.7% of RhB, while the nanocomposite with fabric membrane degraded 82.4% of RhB after 300 min. Polysulfone-based polyaniline- TiO_2 with a hollow fiber membrane was synthesized through a dry-wet spinning

process [112]. The results showed that the polysulfone hollow fibres containing 1.0 wt% of the as-synthesized nanocomposite exhibited a maximum rejection rate of 96.5 and 81.5% for Reactive Orange 16 and Reactive Black 5, respectively. A conductive polypyrrole-polyaniline/TiO₂ nanocomposite was fabricated *via* an *in situ* oxidative copolymerization [113]. The as-fabricated nanocomposite showed a superior photocatalytic degradation of 4-nitrophenol and this improvement was attributed to the conjugated structure, conductivity and the synergy effect among the polymers and TiO₂. A polysulfone-sulfated/TiO₂ nanofiltration membrane showed good efficacy for methylene blue (MB) dye removal with a maximum rejection of 90.4% [114]. A novel and highly efficient α -Fe₂O₃/polypyrrole nanocomposite was successfully designed and fabricated *via* a simple and mild one-step chemical route [115]. The as-fabricated nanocomposite showed a significant photocatalytic degradation toward MB dye under simulated UV irradiation and ambient temperature compared to the bulk Fe₂O₃. The improved photodegradation performance was due to the crystalline nature and mesoporous structure of the nanocomposites as well as the synergetic effect between α -Fe₂O₃ and polypyrrole, which improve the charge separation and recombination rate. The method of preparation and photodegradation activity of polymer/metal oxide nanocomposites are presented in **Table 1**.

Nanocomposites	Method of preparation	Pollutants	References
PVDF/(Ag, Pt)/rGO/TiO ₂	Phase inversion process	Methyl Orange (MO)	[116]
Au/polyaniline/TiO ₂	One-step chemical redox	RhB	[117]
MoO ₃ /polyimide	One-pot homopolymerization	MO	[118]
polyimide/ZnO	Electrospinning and direct ion-exchange process	MB	[119]
Fe ₃ O ₄ /polypyrrole/silver	Wet chemical	MO and Orange II	[120]
polypyrrole/TiO ₂	Reverse microemulsion polymerization	MO	[121]
	<i>In situ</i>	RhB	[122]
	Fractal growth	RhB	[123]
ZnO/polypyrrole/rGO	simple and fast electrochemical	MB	[124]
Polypyrrole/polyvinyl alcohol/TiO ₂	<i>In situ</i> polymerization	RhB	[125]

Table 1. Method of preparation and photocatalytic degradation of metal oxide modified with polymers.

4. Conclusion and outlook

Metal oxide polymer nanocomposites offer great prospects to revolutionize water treatment owing to their unique properties. In this chapter, we have comprehensively reviewed the various synthesis and characterization technique of nanomaterials, unique properties of nanocomposites and progress in water treatment using polymer/inorganic metal oxide nanocomposites. The fundamentals and unique features of metal oxide, as well as the underlying mechanism of the visible light response metal oxide-based photocatalyst, have been

deliberated. The polymer/inorganic metal oxide nanocomposite has been extensively used for the photodegradation of pollutants, ion exchanger, adsorbent, membrane, and photocatalytic disinfection in water treatment. For instance, polymer-based nanocomposites have several intrinsic importance such as high mechanical strength, long-term stability, and low-cost fabrication process, while the inorganic metal oxide possesses superior optical, electronic, magnetic, and catalytic properties. Thus, the hybridization of polymers and metal oxide could enhance several properties of the resultant nanocomposites. In conclusion, the polymer/metal oxide nanocomposite reviewed in this book chapter possesses superior photodegradation activity toward pollutants under simulated light irradiation owing to the large expose area of the nanocomposite, effective migration and separation of charge carriers as well as the strong electrostatic interaction between the catalyst and the pollutants. Moreover, the nanocomposite, exhibit high antibacterial activity, strong affinity toward ions owing to the strong electrostatic interactions between the positively charged ions of the inorganic metal oxide and the lone pair of the organic polymers, excellent regeneration, and adsorption performances, better antifouling property, excellent hydrophilicity due to porosity, larger surface pore size, less microvoids as well as good ion-exchange capacity. Though this book chapter is not a comprehensive, but can give a basic idea about polymer nanocomposites in the various water treatment approaches.

Though considerable development in water treatment using metal oxide and polymer nanocomposite has been accomplished, studies in this area are still at the primary stage and additional advancement is essential. The design and fabrication of materials for water treatment process, particular visible light-response polymer/metal oxide-based photocatalyst materials are significant, but several reports briefly consider only the technical hurdles, high operating cost, and environmental risks. In future, to enhance the practicability of visible light response polymer/metal oxide-based photocatalyst materials in water treatment, several key issues, such as improving the photostability and efficiency of the photocatalyst materials need to be addressed. Moreover, the usage of photocatalytic materials in the photodegradation of pollutants is still a major issue considering the degradation and dissolution of the pollutants, which can hinder their photocatalytic performances. Hence, care should be taken when designing a functional polymer/metal oxide-based material with suitable physicochemical properties. Developing a suitable immobilization approach with cost-effective solid-liquid separation is also important. Currently, an exhausting catalyst during the photocatalysis process will endanger the regeneration of the catalysts and impacts severe effects on the environment as a result of catalysts outflow. To acquire an improved photodegradation efficiency, incorporating different techniques is essential. The accumulation of an enormous amount of theoretical study is also significant to prove an in-depth understanding of the preparation, performances, optimisation, and properties of polymer/metal oxide-based photocatalysts for water treatment.

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