Review



Role and Perspective of Metal-Oxide Based Nanocomposites for Wastewater Treatment: A Review

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Abstract: One among the Global challenges of 21^{st} century is inaccessibility of clean water. In this concern, nanotechnology is rising as one of the most advanced processes for wastewater treatment having/great potential to improve water purification and decontamination efficiency. Among various types of nanomaterials, metal oxides are widely employed in wastewater remediation due to their extremely reduced particle sizes and high specific surface area. However, their limitations, such as a wide band gap and aggregation, which reduce the life time of active species responsible for pollutant degradation, as well as the health risks associated with their release into the environment, require the use of their nanocomposite form in wastewater remediation. This review will summarize efficiencies of metal oxide based nanocomposites (Graphene oxide, ZnO, AgO, TiO₂, CuO) as adsorbent, disinfectant, photocatalyst and membrane filter. It will also give a brief overview of how the wastewater treatment efficiencies of metal oxide-based nanoparticles are enhanced in their nanocomposite form.

Keywords: nanotechnology, wastewater treatment, nanocomposites, adsorption, photocatalysis, membrane filtration, water pollution

1. Introduction

Water pollution is a terrible problem that has become one of the most pressing concerns of the twenty-first century [1-2]. Water safety and quality are critical to society's development and human well-being. However, industrialization and urbanization have resulted in the discharge of effluents into the environment, making some water unfit for consumption [3-4]. The emission of organic dyes and heavy metal ions from industries like paper, leather, and textiles poses a significant challenge due to their potential mutagenic and carcinogenic properties. Several potentially dangerous chemicals have been discovered in aquatic systems [5]. The most prevalent pollutants in industrial waste that must be treated are heavy metals, synthetic and organic colors, and the issue originates from their biodegradation resistance [6-7]. Wastewater contaminated with these organic and inorganic species needs to be treated before being released into the environment in order to comply with environmental standards.

Water impurities encompass a spectrum of organic and inorganic substances, each posing distinct risks to human health and the environment. Organic pollutants, including detergents, fertilizers, phenols, hydrocarbons, pesticides,

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biphenyls, oils, and fats, represent a significant concern due to their potential toxicity and persistence in water sources. Furthermore, pharmaceuticals and personal care products (PPCPs) exhibit resistance to natural biodegradation, resulting in their prolonged presence in water, with concentrations ranging from milligrams per liter (mg/L) to micrograms per liter (μ g/L). In contrast, inorganic contaminants such as arsenic, chromium, cadmium, copper, mercury, zinc, lead, nickel, and various nitrates like fluorides, phosphates, selenides, chlorides, and chromates, also pose substantial threats to water quality and human health. These heavy metals and nitrates are known for their highly toxic properties and can have serious adverse effects on both ecosystems and public health. Despite efforts to mitigate these contaminants, traditional water treatment methods have often struggled to adequately remove persistent low-solubility impurities, emphasizing the urgent need for more effective treatment approaches [8].

To prevent pollution in the environment, cleaning water from various impurities might entail physical, chemical, and biological procedures [9-10]. Biological wastewater treatment is commonly used, but its sluggishness and presence of non-biodegradable pollutants limit its use, and toxic substances can sometimes cause microorganism toxicity [11]. Physical techniques such as filtering can eliminate contaminants by converting phases to one another, but they produce sludge which is hazardous and difficult to dispose [12]. It is crucial to find effective and ecologically friendly ways to get rid of these contaminants. Many techniques, including solvent extraction, evaporation, ultra filtration, and reverse osmosis, are employed for wastewater treatment. But these techniques remove contaminants from water without producing hazardous by-products. The need to find innovative solutions to recover polluted water is underscored by the commitment and shortage of water reservoirs, as well as the restrictions of conventional water handling techniques [13]. This can be accomplished either by creating entirely new ways or by enhancing existing methods through various interventions.

Among the different new technologies, nanotechnology has proven to have enormous potential for wastewater treatment [14-16]. Nanotechnology makes use of nanomaterials that are a few nanometers in size that have some exceptional qualities owing to their minute particle sizes, including a high specific surface area, quick dissolution, strong sorption, high reactivity and superparamagnetism [17]. Nanomaterials can be employed in a variety of water treatment processes, including adsorption, disinfection, catalytic oxidation [13]. Metal-oxide based nanoparticles (CuO, ZnO, TiO₂, AgO, Fe₂O₃, Graphene oxides, etc.) offer unique adsorption, membrane filtration, disinfection, and photodegradation capabilities among other types of nanomaterials [18-19]. As Figure 1 represents that MONCs use different methods to clear wastewater. Even at low concentrations, Metal-oxide-based nanostructures have shown to be efficient adsorbents for heavy metal and semimetal ions. As a result, the adsorption efficiency of metal-oxide-based nanomaterials is frequently higher than that of traditional adsorbents, ranging from 10 to 200 times that of activated carbon, emphasizing their capacity for rapid adsorption of various contaminants [20].



Figure 1. Metal-oxide based nanocomposites for wastewater treatment

1.1 Why nanocomposites

Despite having several attractive characteristics, these metal-oxides have a few drawbacks. The large band gap of metal-oxides, which confines their activity to the UV area alone, and the likelihood of charge carrier recombination reduce the life time of active species responsible for pollutant degradation [21-23]. Other problems include particle loss, complicated post-use recovery processes and associated costs, nanoparticle aggregation with resulting reduction in reactive surfaces, and health risks associated with their discharge into the natural environment [24-25]. As a result, manufactured nanoparticles have been incorporated into support materials, resulting in the production of nanocomposites. These changes reduce nanoparticle loss and aggregation, making it easier to collect them after usage, lowering recovery costs, and making the application procedure safer. In addition, when manufactured nanocomposites are compared to the catalyst alone, various researchers have discovered synergistic results [26-27].

Nanotechnology offers a promising approach to combat drug-resistant microbes, especially through the development of antibacterial disinfectants. Various nanoparticles demonstrate efficacy against bacterial pathogens across medical, agricultural, water resource, and environmental sectors. Nanocomposites, integrating metal and metal oxide nanoparticles alongside environmentally friendly counterparts, provide advantages over traditional antibacterial agents by enhancing penetration and facilitating improved excretion post-treatment. These advanced materials possess potent antibacterial properties, effectively eradicate biofilms, and inhibit bacterial growth through mechanisms such as enhanced cell adhesion and disruption of quorum sensing, modulation of acid production, and attenuation of tolerance. The bactericidal action of nanoparticle-based nanocomposites involves generating reactive oxygen species, controlling ion release, and interacting with bacterial cell membranes. Notable nanoparticles, including iron oxide (I and III), zinc oxide, titanium dioxide, copper oxide, magnesium oxide, nickel oxide, and calcium oxide, exhibit promising antibacterial activity. The physicochemical attributes of nanocomposites, including morphology, size, crystallinity, chemical composition, orientation, solubility, and surface area, significantly influence their antibacterial efficacy. A comprehensive analysis of antimicrobial activity suggests nanocomposites' superiority over individual nanoparticles as disinfectants, likely attributed to inherent physical and chemical modifications enhancing their effectiveness [28].

Nanotechnology is a new field for wastewater treatment that is a better substitute for existing water purification processes such as coagulation, reverse osmosis and precipitation. Nanoparticles, particularly metal-oxide-based nanoparticles have played an essential role in water cleanup processes. It is important to synthesize hybrid nanocomposites by impregnating tiny particles onto large solid particles in order to address all of the issues associated with the usage of metal-oxide nanoparticles, including broad band gap, mess conveyance, aggregation, and loss of such particles [29].

Nonetheless, a large number of review articles have been published that address the importance of nanoparticles in wastewater remediation. However, the use of metal oxide-based nanocomposites (graphene oxide, ZnO, AgO, TiO₂, and CuO) as membrane filters, photocatalysts, disinfectants, and adsorbents in the water purification industry will be assessed in this review. Additionally, it will offer a concise overview of the enhancements in wastewater treatment efficiency achieved through the utilization of metal oxide-based nanoparticles in their nanocomposite configurations.

2. Metal oxide based nanocomposites

Reinforcing material and matrix make up the majority of nanocomposites. Nanocomposites are multi-phase materials with at least one phase that is 10 to 100 nm in size [30]. Figure 2 shows nanocomposites which are discussed in this paper. The properties of nanocomposites in general are determined by the size range of the constituent phases as well as the level of interaction among them [31].

The inorganic metal-oxide provides mechanical and thermal stability, band gap tunability, high carrier mobility, as well as magnetic and dielectric properties in metal-oxide based nanocomposites [32]. Metal-oxide based nanoparticles (CuO, ZnO, TiO₂, AgO, Fe₂O₃, Graphene oxides, etc.) offer unique adsorption, membrane filtration, disinfection, and photodegradation capabilities among other types of nanomaterials. Nanocomposites have many advantages over traditional materials, including high strength, stiffness, endurability, high resistance, low density, corrosion resistance, temperature resistance and gas barrier. Some composites have been shown to be 1,000 times more powerful than their constituent materials [33].



2.1 Types of nanocomposites

There are three main types of nanocomposites.

2.1.1 Ceramic matrix nanocomposites

Ceramic fibers embedded in ceramic matrices are known as composites in the ceramic matrix, or CMCs. Every ceramic material, including carbon fibers, is made up of a matrix and fibers. CMNC matrix raw materials include SiC, Al_2O_3 , and SiN, among others.

For the synthesis of CMNC, a number of approaches have been developed [14-16]. More recently, single-source precursor techniques that involve melting hybrid precursors and then curing and pyrolyzing the fibers have become popular. Conventional powder methods [34], the polymer precursor route, spray pyrolysis [35], and vapor techniques like chemical vapor deposition (CVD) and physical vapor deposition (PVD) are examples of established methodologies. Chemical techniques include the synthesis of templates, the sol-gel process, and colloidal and precipitation techniques [34].

2.1.2 Metal matrix nanocomposites

Metal matrix nanocomposites (MMNCs) are multiphase materials that contain a nanoscale reinforcement material implanted into a matrix of ductile metal or alloy. For MMNC production, metal matrices such as Al, Fe, Mg, Sn, Pb, and W are utilized. The MMNC has the same reinforcements as the CMNC and PMNC. Spray pyrolysis [36], liquid metal infiltration, fast solidification, vapour techniques (PVD, CVD), electrodeposition, and chemical methods-such as colloidal and sol-gel processes are the most often utilized methods in the preparation of MMNC. The one-pot synthesis of carbon dots nanocomposite (CDs), the melt falling-drop quenching method, and gold nanoparticles (AuNPs) nanocomposite are innovative approaches for MMNC [35].

2.1.3 Polymer matrix nanocomposites

The fillers used in PMNCs are known as nanofillers and are categorized as 1D (linear, like carbon nanotubes), 2D (layered, like montmorillonite), and 3D (powder, like silver nanoparticles) [37]. Polymer nanocomposites have been prepared using a variety of techniques. The most popular ones are template synthesis, melt intercalation, in-situ intercalative polymerization, and intercalation of the polymer from solution [38]. The process that allows polymer formation to take place in between the intercalated sheets is called in-situ intercalative polymerization. The process begins with the inflammation of the layered silicate within the liquid monomer. Heat, radiation, the diffusion of an appropriate initiator, or an organic initiator can then start the polymerization process. This method uses a layered polymer matrix without the need for a solvent. With this technique, the synthesis of the clay minerals inside the polymer matrix is achieved by applying an aqueous or gel solution that contains the polymer and the silicate building blocks.

2.2 Fundamental characterization approaches and morphological analysis of MONC

Characterization techniques heavily rely on the analysis of MONCs. It is crucial to determine the morphology and other characteristics of synthesized nanomaterials for in-depth research and utilization. The XRD technique is frequently employed to identify phases and ascertain the crystallite size of each phase within nanocomposites. Nearly all researchers include XRD studies in their reports on synthesized transition metal oxide-based nanocomposites to assess their crystalline quality and phase composition. XRD data presented for graphene oxide/Fe₃O₄ nanocomposits confirms the successful synthesis of the graphene oxide/Fe₃O₄ nanocomposite [39].

Researchers utilize electron microscopes to investigate the size and shape of artificially produced transition metal oxide and other nanomaterials. Among the techniques employed, transmission electron microscopy [36] and scanning electron microscopy (SEM) are common. TEM, for instance, was employed to analyze the size and morphology of synthesized TiO_2 -Ag nanocomposites [40]. Similarly, TEM images were utilized to scrutinize the morphology of CNTs/ TiO_2 nanocomposites [41]. Furthermore, energy-dispersive X-ray spectroscopy (EDX) aids in identifying elements within nanomaterials and synthetic nanocomposites based on transition metal oxides. An examination of Fe₂O₃-Ag nanocomposites using EDX confirmed the presence of oxygen (51.12% by weight), silver (23.25% by weight), and iron (25.63% by weight). Earlier studies also reported FTIR spectra showing a peak at 520 cm⁻¹ related to Zn-O bond vibration and a range of 900-1,500 cm⁻¹ corresponding to extract components on AgZnO nanocomposites' surface [42]. Various combinations of transition metal oxides have been documented for diverse applications. For instance, a flower-like Ni-Co/Fe₃O₄ nanocomposite and CdS-ZnO nanocomposites have been studied for their photocatalytic activity in degrading organic dye (rhodamine B) [37]. Additionally, ZnO/Au nanocomposites with a hollow doughnut-like morphology have been reported. ZnO/Au has exhibited promising attributes in bio-sensing and biomedical applications, among other functionalities [38].

2.3 Reusability of metal-oxide based nanocomposites

The reusable nature of metal oxide nanocomposites is critical in their practical applications, particularly in environmental remediation, catalysis, and sensing. For example, in wastewater treatment, metal oxide nanocomposites like Fe_3O_4 /graphene oxide have shown excellent adsorption capacities for a variety of pollutants. Because magnetic nanoparticles like Fe_3O_4 are present in these nanocomposites, they can be easily separated from the treated water using an external magnetic field after adsorption. Following separation, the nanocomposites can be regenerated using techniques such as thermal treatment or desorption to remove adsorbed pollutants and restore their adsorption capacity. Similarly, metal oxide nanocomposites, such as TiO_2/SiO_2 , have demonstrated promising catalytic activity in a variety of reactions. After successive catalytic cycles, these nanocomposites can be retrieved and reused multiple times without experiencing notable declines in catalytic efficiency, thus mitigating the overall costs and environmental footprint of the process. Consequently, the reusability of metal oxide nanocomposites bolsters their sustainability and economic feasibility across a broad spectrum of applications.

3. Metal-oxide based nanocomposites as nano-adsorbents

Adsorption, a common method for wastewater treatment, offers several advantages over other methods [43]. It is a surface phenomenon wherein the adsorbate gathers on the surface of the adsorbent; this process can occur via either chemisorption or physisorption [40]. To eliminate toxins from wastewater and water, various adsorbents such as lowcost adsorbents, activated carbon, and nanoparticulate adsorbents are often employed. Nanoadsorbents, owing to their large specific surface area, exhibit significantly higher rates of contaminant adsorption compared to powdered activated carbon [41]. Activated carbon, clay minerals, zeolites, montmorillonite, biosorbents, metal-oxide-based adsorbents, as well as trivalent and tetravalent forms of metal phosphates, are just a few examples of the inorganic and organic adsorbents that have recently been utilized in the adsorption process.

Diverse adsorbent techniques encompass a broad array of materials, both inorganic and organic, each with unique advantages and disadvantages. Activated carbon stands out as a commonly utilized adsorbent renowned for its expansive surface area and porous structure, rendering it effective in adsorbing various contaminants. Nonetheless, its costliness

and the need for periodic regeneration pose drawbacks. Clay minerals, such as montmorillonite, provide a natural and abundant alternative. They boast good adsorption capacity and cost-effectiveness but may exhibit limited selectivity and efficiency against certain pollutants. Zeolites represent another category of inorganic adsorbents distinguished by well-defined pores and extensive surface areas. They demonstrate high selectivity and regenerability but may show reduced effectiveness against large molecules and have restricted capacity. Bio-sorbents, derived from natural sources like agricultural waste or biomass, offer an eco-friendly alternative. They are renewable and biodegradable; however, their adsorption capacity and selectivity may vary depending on the source material.

Metal-oxide-based adsorbents, including trivalent and tetravalent forms of metal phosphates, possess unique adsorption properties owing to their chemical composition. While they can be customized to target specific pollutants, their production costs may be prohibitive, and they may not effectively address certain contaminants. Ultimately, the choice of adsorbent hinges on several factors, such as the type of pollutants needing removal, cost considerations, environmental impact, and ease of regeneration. Integrating different adsorbents or combining them with other treatment methods can bolster overall efficacy in wastewater treatment and pollutant elimination [44].

Metal-oxide-based nanomaterials have proven to be highly effective adsorbents for removing pollutants, including heavy metal and metalloid ions, even at low concentrations. The highly reactive surfaces of metal oxides and their nanocomposites accelerate the adsorption process, driven by nanostructured features, active surface sites such as structural flaws and oxygen functions, crystallinity, and other factors. Consequently, the adsorption rates of metal-oxide-based nanomaterials are generally higher than those of traditional adsorbents, being 10-200 times higher than activated carbon. This highlights their potential for rapidly adsorbing pollutants, including heavy metals [20].

Metal-oxide nanoparticles' behaviour in water is said to be influenced by their physical properties and interactions with other water constituents [45]. Nanoparticles agglomerate quickly and precipitate into pure water nanoparticles, which vary their stability under different water conditions [46]. Metal-oxide nanoadsorbents are released into aquatic ecosystems due to the manufacture and application of metal-oxide nanoparticles. Consequently, concerns have arisen regarding the potential threat posed by metal-oxide nanoadsorbents to drinking water supplies [47]. To mitigate the adverse effects of nanoadsorbents on human health and environmental security, nanocomposites must be continuously developed. For instance, the chitosan-coated Fe_3O_4 adsorbent has been proven to be safe and can be utilized in the fruit juice industry for pollutant removal [48]. Table 1 shows list of various metal oxide based nanocomposites's efficiencies as adsorbents for the removal of various pollutants.

3.1 Graphene oxide based nanocomposites

Graphene has significant adsorption capabilities for dyes, organic contaminants, heavy metals, and other substances [29]. Graphene, graphene oxides (GOs), and reduced graphene oxides (rGOs') ability to operate as nano sized adsorbents is greatly dependent on their proper distribution in aqueous phase, as well as their ability to remove diverse pollutants. These nanoadsorbents, however, have severe limitations due to the following reasons (i) massive graphenes have a potential to cluster and re-stack to form graphite during liquid handling [49], (ii) Due to significant electrostatic interactions (i.e., repulsion) between GOs and anionic molecules, GOs and rGOs have a comparatively modest binding affinity for negatively charged substances [50]. Furthermore, other than graphene, the oxygenated groups on the surface of GO sheet are responsible for easy dispersion in water as well as make it capable of functionalization [51-52]. Graphene/GO/rGO-based nanocomposites and hybrids have recently emerged to tackle these limitations through efficient surface functionalization methods. They have garnered significant interest for application in wastewater treatment due to their easy dispersion and stabilization, straightforward sorting and separation, as well as the high accessibility of adsorption sites to enhance adsorption capacity. Examples of such hybrids and nanocomposites include graphene-Fe₃O₄ [53-54], graphene-tannic acid, graphene-carbon nanotubes [55], 3D GOs monoliths [56] and GOs-Fe₃O₄ [57].

Graphene oxide (5 mg) was further functionalized with various fractions (5%, 15%, 35%, and 70%) of dopamine by mass. Ultrasonication was performed in tri-isopropyl-HCl solution at pH 8.5, followed by stirring and centrifugation to release residual GO (lacking surface coating) and dopamine until the formation of a transparent supernatant, resulting in composites of Graphene-polydopamine with respective percentages of dopamine. Their adsorption experiments against methylene blue dye indicated the highest adsorption efficacy of MB by GO/PD 15% (1.89 g/g⁻¹). The adsorption efficiencies of the remaining fractions, 5% (1.3 g/g⁻¹), 35% (1.7 g/g⁻¹), and 70% (0.6 g/g⁻¹), were also greater than their constituents (GO and dopamine). This was attributed to the reduction in precipitation and aggregation, as well as the increase in thickness and roughness of GO sheets due to PD coating, as examined by atomic mass spectroscopy. Surface roughness directly contributes to the rise in surface area for adsorption [58]. GOs-Chitosan, on the other hand, eliminated 70-100 mg/g⁻¹ Pb from synthetic water (100 mg/L⁻¹). The excellent adsorption capacities were attributed to the synchronization of both chitosan and GOs with metals, implying that GOs-chitosan composite hydrogels are wide spectrum heavy metal adsorbents [59].

The graphene/CNT hybrid foam exhibits excellent extraction efficiency for oils and organic solvents owing to its super hydrophobic and superoleophilic features. Its adsorption efficiency varies from 80 to 130 times its own weight, depending on viscosity, density, and surface tension [60]. Compared to GO, the GO-hydrated manganese oxide nanocomposite with equally dispersed MnO_2 nanostructures demonstrated excellent adsorption efficiency for Pb^{2+} ions (500 mg/L) from organic liquid, along with simple isolation of the consumed adsorbent. The adsorption of Pb^{2+} ions was enhanced by the abundant oxygen connectivities of GO and well-distributed hydrated MnO^2 nanoparticles [61-62].

3.2 Titanium oxide based nanocomposites

Variable crystalline structure titanium oxide-based nanomaterials have demonstrated good capacity as adsorbents for rapid removal of bulky ions of various metals [37]. The creation of complexes between metals and oxygenated groups in the TiO₂-GO hybrid enhanced the adsorption potential for the elimination of heavy metal ions due to the flower-like structure of nanocrystalline TiO₂ placed over GO [63]. An innovative 2D adsorbent TiO₂@C-2 generated by a solvothermal technique showed significant adsorption of divalent ions of Pb with an adsorptive removal capacity of 331.7 mg/g⁻¹. According to spectroscopic analyses, hydroxyl groups, electrostatic interaction, and hydrogen bonding are responsible for the TiO₂@C adsorbent's remarkable removal efficacy for Pb²⁺ ions. The TiO₂@C-2's highest surface area could be attributed to TiO₂ ultrathin sheets as well as organic ligands in the sample, providing larger surface active places for effective release of pollutants [64].

Acrylamide-titanium nanocomposites (TiO₂-AM) were utilized as an adsorbent for cadmium elimination from aqueous solutions. At an optimal pH of 8.0, TiO₂-AM had a maximum cadmium binding capacity of 322.58 mg/g, compared to 86.95 mg/g for nano-titanium [65]. The adsorption of Cd^{2+} ions was greatly impacted by the crystal size of anatase TiO₂ nanoparticles. The acrylamide-TiO₂ nanocomposite increased Cd^{2+} ion adsorption capacity (323 mg/L) with minimal interference from contemporaneous positively charged ions (Co^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{+2}) and negatively charged ions (Cl, SO₄₋₂, CO_{3-2}) due to the development of complexes among the amide and the cadmium ions (Figure 3).

The adsorption behavior of TiO_2 towards Cd^{2+} ions in its nanocomposite form with fly ash was studied. The alkaline pH of the adsorbate was adjusted by the TiO_2 nanoparticles treated with fly ash, leading to enhanced adsorption of cationic cadmium ions with 99% removal efficiency in 30 minutes [66]. It was proposed that electrostatic repulsions within the nanoparticles reduced the free-energy requirement for their adsorption considerably on the basis of experimental observations and the fundamental Stern model, resulting in lesser Cd^{2+} ion adsorption [67].



Figure 3. Stepwise preparation scheme of titanium dioxide-acrylamide nanocomposite Source: [65]

3.3 Copper oxide based nanocomposites

CuO is an efficient material for removing arsenic using the adsorption process. Changes in pH values and the presence of opposing anions have a minor impact on arsenic anions' adsorption ability [68]. Over a pH range of 6 to 10, CuO nanoparticles successfully adsorbed arsenite and arsenate ions with maximal adsorption capacities of 26.9 mg/g and 22.6 mg/g, respectively. In polluted water, silicate and sulfate had no effect on the efficiency of CuO nanoparticles for adsorption of arsenate anion, while these ions impeded the adsorption of arsenite by CuO nanoparticles. Furthermore, surface examination of the spent adsorbent revealed arsenite oxidation to arsenate, followed by adsorption onto CuO nanoparticles [69].

For wastewater cleanup, magnetic nanocomposites of copper oxide (Fe₃O₄@CuO) dispersed over graphene oxide (GO) improved the adsorptive elimination of arsenite and arsenate, achieving best adsorption efficiencies of 62.6 mg/g and 70.4 mg/g, respectively. Additionally, the addition of GO inhibited the accumulation of Fe₃O₄@CuO nanocomposite and facilitated the removal of arsenate and arsenite from wastewater. Spectroscopic investigations revealed the adsorptive interface of hydroxyl functionalities of the adsorbent with arsenic ions through complexation processes [70].

3.4 Zinc oxide based nanocomposites

Zinc oxide is a potential adsorbent due to its eco-friendliness, surface-rich chemistry, and strong adsorptive activity [71]. Zinc oxide nanoparticles have been investigated as a promising adsorbent for the remediation of toxic metals from wastewater, particularly Hg^{2+} , with an adsorption capacity of 714 mg/g. Surface adsorption and ion-exchange mechanisms are responsible for the elimination of metals by ZnO nanoparticles [72]. The glutathione-coated hollow zinc oxide, which was synthesized using a microwave method and a polystyrene template demonstrated strong heavy metal ion adsorption, including Hg^{2+} (233 mg/g⁻¹) [4]. The deposited hazardous hexavalent chromium (Cr⁺⁶) was thermochemically transformed to trivalent chromium (Cr⁺³) by the ordered heterogeneous composite of ZnO@TiCN nanourchin.

Furthermore, water hydrolyzed ZnO@TiCN nanourchin generated a hydroxyl functionality across the adsorbent, resulting in slightly acidic pH and the cationic Zn sites. As a result, as the pH rises, the hexavalent species of chromium are quickly removed by adsorption to the negatively charged end of adsorbent surface [73].

3.5 Silver oxide based nanocomposites

One of the most widely used metal-oxide nanocomposite adsorbents is silver oxide [74]. One such nanocomposite (trimetallic nanocomposite of AgO/MgO/FeO@Si₃N₄) has been prepared for the elimination of tetracycline from aqueous solution.

Metal-oxide based nanocomposite	Target pollutant	Nanocomposites as adsorbents	Treatment efficiency (Maximum adsorption capacity)	References
			Percentage/concentration %/mg/g ⁻¹	
ZnO based nanocomposite	Pb (II)	Zinc oxide-coated nano porous carbon sorbent	522.8 mg/g ⁻¹ , (97.25% at pH 6)	[75]
	Pb (II)	Zinc oxide/talc nanocomposite	48.3 mg/g ⁻¹	[76]
	Cu (II) and Ph (II) ions	Zinc oxide/clay minerals nanocomposite	Cu (II) = 83.30 mg/g^{-1} and Ph (II) = 88.50 (at pH 4)	[67]
	lead Pb (II) and arsenic as (V)	Zeolite/zinc oxide nanocomposite	Pb (II) = 47.6 mg/g^{-1} and As (V) = 45.8 mg/g^{-1} (93% and 89%) at pH 4	[77]

Table 1. Metal oxide based nanocomposites's efficiencies as adsorbent for the removal of various pollutants

Table 1. (cont.)

Metal-oxide based nanocomposite	Target pollutant	Nanocomposites as adsorbents	posites as Treatment efficiency bents (maximum adsorption capacity)	
	Toxic phenols	Zinc oxide-doped prussian blue nanocomposite	97.25% Maximum adsorption capacity at pH 6.5	[78]
CuO based nanocomposite Ag/AgO based nanocomposites	Acid orange, methylene blue (MB), ciprofoxacin, rhodamine B and atrazine	BC-CuO	$\begin{array}{c} \text{methylene blue (MB)} = 99.6\%,\\ \text{O} \qquad \qquad \text{acid orange} = 100\%, \text{ rhodamine B} = 100\%,\\ \text{atrazine} = 100\% \text{ and ciprofoxacin} = 78.27\% \end{array}$	
	lead (Pb ²⁺⁾ ions	Kaolinite coated with copper oxide	856 mg/g ⁻¹ at pH = 6.05	[80]
	0.1 mM 4-Nitro phenol	0.1 mM Ag/reduced graphene oxide 52 mg/g ⁻¹		[81]
	Adsorption of tetracycline	AgO/MgO/FeO@ Si ₃ N ₄ nanocomposite	172.41 mg/g ⁻¹ at pH = 8	[28]
TiO ₂ based nanocomposites	Adsorption of anionic dye	Silver-Graphene Oxide nanocomposite	(222.22 mg/L)	[82]
	Adsorption of As (III) and As (V)	II) and Smectite-titanium oxide nanocomposite 52.11 mg/L maximum removal at pH =		[83]
	As (III) As (V)	m-TiO ₂ - α Fe ₂ O ₃ 80% 99%		[84]
Graphene oxide based nanocomposites	Copper	GOs-Fe ₃ O ₄	$= 18.3-25.6 \text{ mg/g}^{-1}$ (pH 2-11)	[85]
	Uranium metal (U)	GOs-Fe ₃ O ₄	= 68.5-106 mg/g ⁻¹ (pH 2-12)	[86]
	Ciprofloxacin	GOs-sodium alginate	55.5-86.1 mg/g ⁻¹ (pH 2-12)	[87]
	Methylene blue, Eosin Y	GOs-chitosan (GO-CS10)	Methylene blue = 390 mg/g^{-1} Eosin Y = 326 mg/g^{-1}	[59]

4. Metal oxide based nanocomposites as photocatalyst

The oxidation or reduction of pollutants in the presence of light and a catalyst is known as photocatalysis. In water purification, photocatalytic materials including semiconductors as well as metal oxides such as TiO_2 are used to remove contaminants from wastewater [88-89]. Due to their potential photoactivity, wide band gap, lack of toxicity, and low cost, they have been described as ideal photocatalysts. Table 2 shows the efficiencies of various metal oxide-based nanocomposites as photocatalysts for the removal of various pollutants.

4.1 Titanium oxide based nanocomposites

 TiO_2 is widely utilized nano photocatalysts due to the chemical stability and great reactivity under UV light [90]. Numerous studies on the use of TiO_2 as a photocatalyst for diverse applications such as organic pollutant degradation, hydrogen generation from water splitting, and air purification have been published [91-93]. There is an increased attention on synthesis of TiO_2 nanocomposites in order to increase photocatalytic efficiency of TiO_2 nanoparticles [94].

Under visible light irradiation, the produced BiOBr-TiO₂ nanocomposite exhibits good photocatalytic action for the destruction of rhodamine B. This is owing to the synergistic action of TiO_2 and BiOBr nanocomposite, which has great potential for water purification [95]. Camphene-based freeze-drying was utilized to make TiO_2 -ceramic nanocomposites, which were subsequently used to photo-degrade insecticides. Mechanical stability, photocatalytic activity, and porosity were all greatly increased in these composites. The herbicides Atrazine, Thiobencarb, Dimethoate, Dipterex, Lindane

Bentazone, and Malathion were effectively photo-degraded by the hierarchical porous TiO₂-ceramics.

Camphene-based freeze-drying was utilized to produce TiO₂-ceramic nanocomposites, which were subsequently employed to photodegrade insecticides. Mechanical stability, photocatalytic activity, and porosity were significantly enhanced in these composites. The herbicides Atrazine, Thiobencarb, Dimethoate, Dipterex, Lindane, Bentazone, and Malathion were effectively photodegraded by the hierarchical porous TiO₂-ceramics [96].

4.2 Graphene oxide based nanocomposites

Photocatalytic degradation of organic contaminants was investigated using/graphene nanocomposites with various metal-oxides including ZnO, MnO_2 , TiO_2 and others. Despite the fact that TiO_2 is most commonly used as a photocatalyst, but it has few a limitations (Figure 4).



Figure 4. Limitations in photocatalytic activity of TiO₂ nanoparticles

The properties of graphene oxide that make it a suitable choice for enhancing the photocatalytic activity of its nanocomposite form are to enhance the lifetime of the photocatalyst by avoiding corrosion and the release of nanoparticles into water. Another reason is that the quenching of pollutants is increased with p-p stacking among organic pollutants and the cyclic ring of graphene oxide [97]. The development of a graphene-TiO₂ composite photocatalyst can address these challenges because graphene has higher electron mobility, which improves electron transport and suppresses electron-hole recombination. Furthermore, using a graphene-TiO₂ composite may prevent the agglomeration of TiO₂, resulting in a larger surface area and more active sites for pollutant degradation. This enhances the rate of pollutant degradation while requiring a smaller amount of graphene-TiO₂ composite-based photocatalyst. Additionally, graphene boasts high thermal conductivity, a large specific area, improved charge carrier mobility, and superior mechanical strength [98].

 TiO_2 /graphene oxide composite for the photo catalyzed degradation of methylene blue has been prepared [99]. In the presence of the composites, rather than pure TiO_2 , greater adsorption and photocatalytic performance were achieved under both UV and visible radiation. A schematic illustration of the photocatalytic degradation of dye is represented in Figure 5. The degradation of methylene blue also investigated the photocatalytic activity of reduced graphene oxide-P25 composites, showing a greater conversion of methylene blue than bare P25 [100].

In comparison to ZnO nanoparticles, the ZnO-rGO nanocomposite, which has exceptional structural characteristics, successfully absorbed the Rhodamine B dye. Furthermore, the adsorbed rhodamine B was subsequently destroyed by ZnO-photocatalytic rGO's activity [101].



Figure 5. Schematic illustration of photocatalytic activity of GO-TiO₂ nanocomposite

4.3 Zinc oxide based nanocomposites

In the degradation of various organic pollutants, Zinc Oxide (ZnO) may exhibit comparable photocatalytic performance to the highly promising Titanium Dioxide (TiO₂) material. ZnO is believed to surpass TiO₂ in terms of photocatalytic activity due to its higher quantum efficiency. Moreover, previous studies have demonstrated ZnO's capability to effectively mitigate organic pollutants, positioning it as one of the most promising semiconductors across a wide range of applications, including wastewater treatment and biological research. The photocatalytic properties of ZnO have been extensively explored, mirroring TiO₂'s broad band gap and making it a compelling candidate for photocatalysis [102]. Despite the fact that zinc oxide can oxidise As(III) to As(V), its adsorption effectiveness is modest due to its small total active surface area [103].

Integrating a specialized adsorbent with superior adsorption capacity into the photocatalyst can effectively address the limitations of the photocatalyst. In a recent study, a photosensitizer/oxidant nanocomposite of $ZnO/Na_2S_2O_8$ was employed to accelerate the photo-degradation of a wide range of pesticides in wastewater using natural sunlight. By enhancing the oxidative potential of ZnO, the addition of $Na_2S_2O_8$ reduced the time required for photocatalytic pesticide degradation [104]. Copper-doped ZnO nanorods were employed for the removal of organophosphorus pesticides by effectively delaying the recombination of electron-hole pairs. This innovative approach proved to be highly recyclable and achieved a remarkable 96.97% removal rate of diazinon [105].

4.4 Copper-oxide based nanocomposites

ZnO nanocomposite (CuO-ZnO) exhibited twice the photocatalytic activity for degrading textile dyes compared to bare ZnO nanoparticles, when exposed to visible light. The incorporation of CuO into ZnO nanomaterials introduces structural flaws and stoichiometric deficiencies, leading to alterations in band gap energy and an enhanced photocatalytic activity of the CuO-ZnO nanocomposite. Furthermore, the presence of exogenous electron acceptors such as H_2O_2 , peroxodisulfate, and peroxomonosulfate accelerated the photocatalytic decomposition of textile dyes [106]. Table 2 shows the efficiency of CuO-ZnO for the removal of Congo red dye.

Metal-oxide based nanocomposite	etal-oxide based Target pollutant Nanocomposites as photocatalysts		Treatment efficacy mg/g ⁻¹		References
	Nonylphenol	$TiO_2 + PVDF$	85	-	[87]
TiO ₂ based nanocomposite	Escherichia coli	TiO ₂ /rGO from UV-assisted GO reduction	55		[85]
	Escherichia coli	Ag-TiO ₂ nanorods/GO	70		[85]
	Methylene blue	PVA/TiO ₂ /graphene MWCNT	100 (recorded in the first cycle)		[107]
Graphene oxide	Reactive black 5	GO-MnO	70		[108]
based nanocomposite	Methylene blue	GO-SnO2	89		[109]
	Brilliant green	GO/CuO	98.8		[110]
	Orange II dye	$ZnFe_2O_4 + persulfate$	-	191.8 at (pH = 6)	
ZnO based nanocomposites	Congo red dye	ZnO/CuO	95		[111]
	Congo red dye	ZnO/CuO	83		[112]
CuO based nanocomposites	ortho and para nitrophenols (NP)	Monoclinic CuO/R-GO	100		[113]
	direct red 80 azo dy	ZnO/CuO	97.9 (removal after 60 min)		[114]
Silver-oxide based nanocomposite	Ag ₂ O-WO ₃ (tungsten oxide)	Methylene blue rhodamine B	90.8% 87.25%		[115]

Table 2. Metal oxide based nanocomposite's efficiencies as photocatalyst for the removal of various pollutants

5. Metal oxides based nanocomposites as membrane-filters



Figure 6. Types of membrane-filtration on the basis of pressure difference

Membrane filtration is a process that involves the isolation of substances using a semipermeable membrane, allowing some constituents to pass through while rejecting others. This technique is considered environmentally sustainable and effective for removing pollutants from wastewater, such as heavy metal ions, as it minimizes the use of chemical reagents and generates minimal wet sludge [116-117]. These membrane-based procedures involve the phenomena of pressure difference working as a driving force as shown in Figure 6. Microfiltration, Nanofiltration (NF), Ultrafiltration (UF) and Reverse Osmosis (RO) are types of pressure-driven membrane techniques that have been shown to be successful in removing organic micropollutants [118-119].

Various nanoparticles have been used in the establishment of innovative nanocomposite membranes used for water remediation, including silver (Ag) [120], zinc (ZnO) [121], titanium (TiO₂) [122], copper oxide (CuO) [123], and graphene oxide (GO) [124]. Table 4 shows a list of various metal oxide based nanocomposites's efficiencies in the removal of various pollutants by using the technique of membrane filtration. Adding inorganic particles to nanoparticles (NPs)-based membranes resulted in a low-fouling method [125], however, they have limitations infiltration mechanisms. In order to avoid these limitations composite membranes are normally formed by dispersing the NPs into the matrix/ polymer, and they are also a useful tool for enhancing the working of polymeric membranes, such as selectivity and penetrability [126].

Selectivity, anti-fouling properties and permeability are the most significant characteristics of polymeric membranes that are modified with this incorporation and are largely influenced by the size, type and quantity of nanoparticles, and above all, pattern of addition of nanoparticles to polymeric matrix. Table 3 shows properties of various metal oxide based nanocomposites as nanofilters for their role in nanofiltration.

Metal-oxide (nanofilters)	Property	
TiO ₂	Pollutants removal ability, stability in harsh condition, anti-fouling and less expensive	[127-129]
Fe_3O_4	Magnetic enhancement of heat stability of polymers	[130]
Ag/AgO	Antibacterial, anti-biofouling disinfection and wastewater filtration	[131-134]
GO	Hydrophilic performance and improved water flux, higher water permeability and anti-biofouling capability	[135]
ZnO	Thermal stability and hydrophilicity properties	[136]

Table 3. Properties of metal oxide based nanocomposites as nanofilters

Actually, the manufacture and usage of these membranes is one among the recent applications of nanotechnology in membranous filtration for water remediation [137]. Another key problem in establishment of high-performance nanocomposite membranes is even dispersion of nano constituents in polymeric matrix. Strong interfacial contacts between nanoparticles and weak nanoparticle-polymer interactions cause nanoparticles to agglomerate. Due to poor nanoparticle distribution and agglomeration, nanocomposite membrane filtration may be limited [138].

Catalytic ozonation with CCMs proves highly effective in breaking down and eliminating organic pollutants from water, including a dye used as a model pollutant, as well as residual organics in secondary wastewater effluent. When compared to ozonation alone, coupling ozonation with membrane filtration significantly improves organic removal efficiency. For instance, while the ceramic membrane without catalyst coating achieves approximately 30% removal, the CCM-coated membrane achieves over 80% removal at the same ozone dosage. Furthermore, membrane catalytic ozonation effectively controls membrane fouling during ultrafiltration of the secondary effluent. This process generates more hydroxyl (•OH) free radicals compared to ozonation alone, as confirmed by the hydroxyl quenching test, leading to enhanced organic degradation (Figure 7). Additionally, catalytic ozonation within the membrane reactor proves instrumental in mitigating membrane fouling. Overall, ceramic membrane-based catalytic ozonation emerges as a promising approach for efficiently eliminating toxic and persistent organic pollutants from both water and wastewater [139].



Figure 7. Ceramic membranes for catalytic ozonation of organic pollutants in wastewater treatment

5.1 Graphene oxide nanocomposites

Graphene oxide nanoparticles, among other Metal-oxides, are commonly used in membranes to improve hydrophilic performance and water flux. Due to its electrostatic repulsion and hydrophilicity, the GO membrane has a better water permeability and anti-biofouling performance. The improved activity in terms of anti-fouling and hydrophilicity after incorporating/gO into a PVDF membrane matrix by mixing was studied. However, the creation of nanoparticle agglomerates restricts GO's antibacterial potential by reducing interaction with other bio constituents such as DNA and proteins at relatively high additive concentrations [140].

In addition, when dealing with proteins like BSA, the antibacterial action of GO integrated membranes is reduced due to non-covalent adsorption [85]. As a result, it is required to change the GO surface in order to improve scattering in polymer membrane matrices. The effects of GO merged with one-dimensional oxidized CNTs (GO-OMWCNTs) on the permeability and antifouling process of PVDF nanocomposite membranes were also studied [141].

5.2 TiO₂ based nanocomposites

Titanium dioxide (TiO_2) is a non-water repellent inorganic nanoparticle extensively employed in the manufacturing of nanocomposite UF membranes and reason behind it is high level of its photocatalytic activity and stability [142-143]. Many investigations have shown that covering TiO_2 nanoparticles with a comparatively low surface energy constituent in form of composite improves their dispersity and photocatalytic performance in solvents, preventing particle agglomeration at high concentrations [144].

It was studied that the performance of TiO_2 nanocomposite membranes mixed with sulfonated PES (SPES/TiO₂) and found a significant modification in membrane hydrophilicity due to the high level of hydroxyl in the nano-TiO₂ surface [145]. A significant improvement in the nanocomposite membrane's rejection properties has been noticed. The self-assembly of nano-TiO₂ and SPES with ether bonds, sulfonic groups, and sulfuryl groups is thought to be the cause of this phenomenon.

5.3 ZnO based nanocomposite

The scattering of the ZnO NPs in the solvent, which provides a comparatively greater surface area for NPs-polymer interactions, can also be ascribed to the nanocomposite membranes' exceptional heat stability [146]. The hydrophilicity

and heat stability of nanocomposite membranes improve with increasing ZnO concentration [136]. A poly(1-vinylpyrrolidone-coacrylonitrile)-ZnO and poly(ether sulfone)-ZnO ultra filtration membrane with strong antibacterial performance and water flow were developed [147]. Both membranes have better water flux, significant antibacterial activity, and antifouling properties, according to the findings. A self-assembly technique was used to create hybrid membranes for reverse osmosis by TiO_2 particles and aromatic polyamide thin films [148]. When the nanocomposite was exposed to UV light, it had a higher photocatalytic bactericidal efficacy than when it was exposed to darkness or light.

Metal-oxide based nanocomposites	Target pollutant	Nanocomposite	Treatment effi %	cacy mg/g ⁻¹	References
Graphene oxide based	Decolorization of distillery effluent	Graphene oxide + (PES) polyethylene sulfone	54		[85]
nanocomposites	mono/-divalent salt	GO + PDA (polydiacetylene)	6-46		[141]
	Na ₂ SO ₄ MgSO ₄ Methylene blue	TiO_2 + anodic aluminum oxide membrane (AAO)	43 35 ~96		[149]
Titanium oxide based	Bisphenol A	TiO ₂ + PVD (Polyvinylidene Fluoride)	85%		[150]
nanocomposites	As Cd Pb	Al-Ti ₂ O ₆ + PS (polysulfone)	96 98 99		[151]
	dye-oil emulsion.	GO-TiO_2 + polydopamine composite	above 98		[152]
Zinc oxide based	Copper ions	ZnO + PVD		34.96	[153]
nanocomposites	Humic acid	ZnO + polyether sulfone	96.34		[153]
Silver oxide based nanocomposites	Na_2SO_4 Mg_2SO_4 Methylene blue methylorange	Ag-MOF + polyamide	84.1 73.1 87.8 95.4		[154]
Copper-oxide based nanocomposites	Bovine serum albumin (BSA)	CuO + PES	97		[155]
	Humic acid (HA)	CuO + PES	95		[156]
	BSA	CuO/ZnO + PES	95		[157]
	$egin{aligned} { m Na_2SO_4}\ { m NaCl}\ { m Cu}^{+2} \end{aligned}$	CoFe ₂ O ₄ /CuO + PES-PVP (polyvinylpyrrolidone)	95 72 85		[158]

Table 4. Metal oxide based nanocomposite's efficiencies as membrane filters for the removal of various pollutants

6. Metal-oxides based nanocomposites as disinfectants

The prevalence of microbial infections that can spread to people and other animals, resulting in serious public health effects, is a cause of concern, particularly during outbreaks. In domestic water storage tanks, for example, several microbial pathogens such as Salmonella typhi, Vibrio cholerae, *E. coli*, Staphylococcus aureus and certain enteric viruses are found [159]. In response to the negative health effects of polluted water due to microbes on people, a variety of treatment methods have been used to make water fit for human consumption. Chemicals such as chlorine are used in several of these approaches. Chlorine, along with a variety of other oxidizing agents (chlorine dioxide, chloramines, hydrogen peroxide and ozone), is widely employed in the disinfection of drinking water. In the water business,

chlorination has long been the most popular approach, as it provides both main and residual decontamination [160]. However, chlorine has a number of disadvantages, including its short-term efficacy, corrosiveness, and toxicity [161].

To come up with a safe solution nanocomposite is a potential water decontaminator and alternative for present chemical disinfectants, thanks to the development of nanotechnology [162]. By offering/good adherence to cells, acid generation, quorum detection, and tolerance, nanocomposites that consider biofilm removal restrict growth. The formation of responsive oxygen species, the influence of the bacterial cell membrane and the discharge of ions are all included in bactericidal action of nanoparticle-based nanocomposites. Antibacterial activity was demonstrated in Metal-oxides such as iron oxide (I & III), titanium dioxide, zinc oxide, copper oxide, nickel oxide, magnesium oxide and calcium oxide. The size, shape, orientation, crystallinity, solubility, chemical composition as well as surface area of nanocomposites all play a role in their antibacterial action [163]. The inhibitory zone grew larger as the concentration of Ag-NPs increased, and Ag-NPs-PES membranes prevented biofilm growth [153].

The magnetic Fe_3O_4 -AgBr nanocomposite has been utilized as an effective catalyst for the inactivation of bacteria in drinking water when subjected to light-emitting diode (LED) lamp irradiation. The findings indicate the ability of Fe_3O_4 -AgBr to deactivate both S. aureus and *E. coli* bacteria. Notably, bacterial inactivation occurs under anaerobic conditions, implying that Fe_3O_4 -AgBr generates reactive oxygen species (ROS). This process is facilitated by the oxidation of H_2O_2 produced from the conduction band of Fe_2O_3 and the direct oxidation of H+ ions from AgBr, as depicted in Figure 8 [164].



Figure 8. Fe₂O₃-AgBr nanocomposites: A proposed mechanism for schematic representation of *E. coli* inactivation [165] Proposed mechanism for schematic representation of *E. coli* inactivation by nanocomposites. (A higher resolution/ colour version of this figure is available in the electronic copy of the article)

6.1 Zinc oxide based nanocomposites

The ZnO nanoparticles enhanced antibacterial activity in their nanocomposite form. The thickness of cell wall and presence of plasma membrane in gram +ve bacteria are responsible for higher antibacterial activity of Chitosan (CS)/ZnO Nanocomposite. Although, gram negative bacteria have cell walls, but their constituent peptidoglycan is among plasma membrane and external membrane. CS/ZnO was capable of reducing the bacterial development at minor concentration. The experimental results confirmed the strong biocidal capacity is due to synergetic effect of Chitosan and ZnO [166]. Chitosan is a +ve charged polysaccharide and capable of fascinating the -ve charged membrane around bacteria, however, ZnO aggravates reactive species of oxygen resulting in enhancement of their association in nanocomposites [155, 167].

6.2 Titanium oxide based nanocomposites

The major driving force behind all of TiO_2 's applications is its photocatalytic characteristic. When photoexcited with photons with energies larger than or equal to the band gap energy of TiO_2 , electron hole pairs are generated, resulting in the induction of redox processes at the TiO_2 surface, leading to the creation of reactive oxygen species (ROS). The bactericidal activity of this ROS is based on its ability to attack the microorganism's cell membrane [168]. Many people have used silver-TiO₂ nanocomposite in photo-catalytically destroying water-polluting microorganisms, as well as water-polluting dyes and heavy metals. Several ways have been used to create silver-TiO₂. TiO₂-ZnO is also used for removal of Escherichia coli from wastewater having treatment efficiency of 10.73 mm as shown in Table 5.

The photo-decomposition of *E. coli* under solar and visible light irradiation was investigated using a nanocomposite film of Ag-TiO₂ developed by using sol-gel methodology [169]. The antibacterial activity of the as-prepared nanocomposite film was found to be 5.1 times higher than anatase-TiO₂ (in the dark) and 6.90 and 1.35 times higher than anatase-TiO₂ and Ag/a-TiO₂ when exposed to sunlight respectively and the film's durability was 11 times greater than that of Ag/a-TiO₂ films. This nanocomposite can be used to decontaminate water and is long-lasting and effective antibacterial nanocomposite material.

6.3 Graphene oxide based nanocomposites

In real-world applications, it's critical to speed up the procedure to reduce disinfection time. Various nanomaterials such as metal nanoparticles, polymers, photocatalyst and biocidal chemicals are functionalized with graphene using covalent and non-covalent techniques to achieve this goal, and the resulting nanocomposites will have increased antimicrobial activity. Unsurprisingly, the metal NPs/graphene nanocomposites outperformed the single molecule in terms of antibacterial activity. Metal NPs/graphene nanocomposites have increased antibacterial activity for at least three reasons. For starters, using/gO or rGO as an attaching substrate could reduce nanoparticle aggregation. The interaction of graphene materials with bacterial cells could also be a factor. Adsorption characteristics of GO or rGO towards bacterial cells were discovered. Furthermore, GO or rGO having a greater lateral size may be able to catch bacteria in suspensions [170]. The contacts between active metal NPs and cells in the nanocomposites enhanced as a result of these factors. Furthermore, metal ion release near the cell results in a larger local accumulation of metal ions, resulting in enhanced bactericidal activity [171]. The antibacterial activity of the produced nanocomposites was clearly increased by the attachment of antimicrobial metal NPs to graphene. The synergistic contact between graphene materials and metal NPs especially Ag is responsible for the increased antibacterial activity (Figure 9).



Figure 9. Antibacterial activity of GO based nanocomposite (GO-Ag)

6.4 Silver oxide based nanocomposites

Materials based on Ag have antibacterial qualities that make them suitable for a variety of applications, involving water treatment and medical device disinfection. There have been some reports of incorporation of silver nanoparticles into polyethylene (PE) membrane for medical purposes and the production of silver nanosized fibers of PE has been reported [172]. The antibacterial activity of Ag-NPs was also discussed [173]. The size, shape, and chemistry of the particles, as well as their size, shape, and chemistry, all influence their activity. Because of a synergistic influence between release of Ag^+ ions and direct particle-specific biological effects, Ag-NPs typically inhibit bacterial activity. In addition to it, Ag-NPs can adhere to bacterial cells, reducing their permeability and respiration. However, particles might damage the cell membrane, results in cell lysis. The nanoparticles of Ag can then enter the cytoplasm of the bacteria and cause DNA damage. [125, 174-175].

The integration of Ag-NPs into the surface of polyethylene sulphonated (PES) membranes with vitamin C as a reducing agent was also reported earlier [176]. A method for visualizing the anti-biofouling performance of immobilized metallic Ag^0 and ionic Ag^+ silver on chitosan (CS) membranes as also described [177]. Further, titanium, copper and silver oxide based nanocomposites antimicrobial properties are mentioned in Table 5.

Metal-oxide based nanocomposite	Target pollutant (microbes)	Nanocomposites as disinfectant	Treatm %	ent efficiency IZD (mm)	References
Graphene-oxide based nanocomposite	E. coli	AgNPs-rGO	100		[178]
	E. coli	TiO2-GO	100		[178]
	E. coli, C. albicans, S. aureus, S. epidermidis	AgNPs-GO	89 78 81 76		[179]
Ag/AGO-based nanocomposite	Escherichia coli and staphylococcus aureus	PVB polymer/silver nanoparticle nanocomposite		1.93 1.59	[180]
	Escherichia coli, bacillus subtilis, S. aureus and pseudomonas aeruginosa	Chitosan-silver oxide nanocomposite		16, 20, 23 24	[181]
	Escherichia coli,	Ag/rGO	99.99		[182]
	Escherichia coli	Ag/GO	100		[183]
TiO ₂ -based nanocomposite	Escherichia coli	Silver-titanium dioxide nanocomposite	90 (240-min)		[184]
	Escherichia coli	TiO ₂ /ZnO nanocomposites		10.73 mm	[185]
CuO-based nanocomposite	E. coli	ZnO-CuO		9 mm	[186]
	Shigella sonnei, escherichia coli, salmonella typhi, pseudomonas aeruginosa	Copper-chitosan nanocomposites		8 mm, 8.5 m, 8 mm, 7.3 mm	[187]
ZnO-based nanocomposite	Escherichia coli, bacillus sp.	Chitosan-zinc oxide (CS/ZnO)		<i>Bacillus sp.</i> at 100 (µl) 4 mm, Escherichia coli at 120 (µl) 3 mm	[188]
	Escherichia coli, S. aureus	ZnO/TiO	90%, 99%		[189]

Table 5. Metal oxide based nanocomposite's efficiencies as disinfectant for the removal of various pollutants

IZD = inhibitor zones diameter

7. Conclusion

In this era of nanotechnology, metal oxide based nanoparticles have shown great accomplishment for monitoring water treatment challenges for making future advancement. Despite having a number of attractive characteristics, these metal oxide based nanoparticles are replaced with their nanocomposites in wastewater treatment due to likelihood of charge carrier recombination, confinement of reactivity to UV region and nanoparticle aggregation which reduces the lifetime of active species responsible for pollutant degradation with resulting health risks associated with their discharge into the natural environment. This comprehensive review summarized wastewater treatment efficiencies of metal oxide based nanocomposites (TiO₂, AgO, Fe₂O₃, CuO, Graphene oxide) as adsorbent, photocatalyst, membrane filter and disinfectant. It also gave brief overview of modification in their treatment efficiency with use of their nanocomposite form. It is concluded that among these metal oxides, graphene oxides are most widely used in wastewater treatment procedures because of their wider adsorption sites, antifouling properties, broadening of spectrum and p-p stacking. Graphene in its nanocomposite form is more efficient due to avoidance of aggregation, corrosion and improved charge carrier mobility which in turn suppresses electron hole recombination. For photocatalytic wastewater treatment graphene modified TiO₂ nanocomposites are more efficient than bare TiO₂ nanoparticles due to confinement to UV region and low adsorption capacity for hydrophobic contaminants. In nanocomposite forms selectivity, anti-fouling and permeability are the most significant characteristics of polymeric membranes responsible for enhanced treatment efficacy. Because of antimicrobial activity, silver oxide based nanocomposites are widely employed as disinfectant and in membrane filtration procedures. Nanomaterial technologies such as adsorption, nanostructured catalytic membranes, and others are highly efficient, low-energy, and environmentally friendly procedures, but they are not inexpensive, and they have yet to be employed commercially to cleanse wastewater on a big scale.

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Author contributions

All authors have made significant contributions to the interpretation of data. Schrish Fatima and Dr. Naeem Abbas were responsible for writing and preparing the final draft, with input and review from all co-authors. All authors have approved the final version of the manuscript and agreed to be responsible for all aspects of the work.

Conflict of interest

The authors declare there is no conflict of interest at any point with reference to research findings.

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