

Review

Recent Advances in the Adsorption of Different Pollutants from Wastewater Using Carbon-Based and Metal-Oxide Nanoparticles

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Abstract: In recent years, nanomaterials have gained special attention for removing contaminants from wastewater. Nanoparticles (NPs), such as carbon-based materials and metal oxides, exhibit exceptional adsorption capacity and antimicrobial properties for wastewater treatment. Their unique properties, including reactivity, high surface area, and tunable surface functionalities, make them highly effective adsorbents. They can remove contaminants such as organics, inorganics, pharmaceuticals, medicine, and dyes by adsorption mechanisms. In this review, the effectiveness of different types of carbon-based NPs, including carbon nanotubes (CNTs), graphene-based nanoparticles (GNPs), carbon quantum dots (CQDs), carbon nanofibers (CNFs), and carbon nanospheres (CNSs), and metal oxides, including copper oxide (CuO), zinc oxide (ZnO), iron oxide (Fe₂O₃), titanium oxide (TiO₂), and silver oxide (Ag₂O), in the removal of different contaminants from wastewater has been comprehensively evaluated. In addition, their synthesis methods, such as physical, chemical, and biological, have been described. Based on the findings, CNPs can remove 75 to 90% of pollutants within two hours, while MONPs can remove 60% to 99% of dye in 150 min, except iron oxide NPs. For future studies, the integration of NPs into existing treatment systems and the development of novel nanomaterials are recommended. Hence, the potential of NPs is promising, but challenges related to their environmental impact and their toxicity must be considered.

Keywords: carbon-based nanoparticles; metal-oxide-based nanoparticles; adsorption; pollutants; wastewater treatment



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1. Introduction

Water is a fundamental resource that plays a crucial role in sustaining life, and ensuring its cleanliness is essential. Water pollution emerges as a pressing global concern for the current generation, extending beyond human impact to affect all forms of life [1]. The sources of pollutants in water bodies originate from either natural or anthropogenic sources, including industrial, agricultural, and daily human activities [2]. They are classified into organic pollutants, inorganic pollutants, and biological pollutants [3,4]. Inorganic pollutants are chemical substances of non-biological origin that pose a significant threat to aquatic flora and fauna by entering and accumulating in the food chain, thereby exerting adverse effects.

They are classified into different categories, such as toxic metals, metal compounds, and inorganic salts [5]. Organic pollutants comprise pesticides, dyes, and phenols, which are mainly from the pharmaceutical and agricultural industries, whereas biological pollutants are classified as viruses, bacteria, and protozoa [6].

Nanotechnology in Wastewater Treatment

Different treatment techniques can effectively remove pollutants, chemicals, and pathogens. Traditional water treatment involves various methods such as filtration, coagulation, and flocculation for gathering and removing impurities, sedimentation, and disinfection using processes like chlorination, UV irradiation, and ozonation [7]. In addition, advanced techniques such as reverse osmosis removal, ion exchange, and desalination are used to treat wastewater. The development of nanoscience and nanotechnology offers a promising solution to the drawbacks associated with conventional water treatment [8,9]. Particles with diameters smaller than 100 nm are called nanoparticles (NPs). Nanomaterials, including NPs, with their unique properties, such as high adsorption capacity, catalytic activity, and reactivity, have gained attention for their effectiveness in water and wastewater treatment [10,11]. Recent advancements in nanomaterials, including nano photocatalysts, nanomembranes, and nano sorbents, provide diverse tools in the field of water treatment [12]. Therefore, nanotechnology serves not only as a catalyst for advancing the field but also introduces innovative pathways to enhance pollutant removal efficiency [13]. Adsorption is a fundamental physical technique used to remove pollutants from the environment that depends on the active involvement of nanomaterials. This method has several advantages compared to other mentioned methods, which are explained in Table 1.

Table 1. Different nanotechnology methods for water treatment.

Method	Types of Pollutants	Pros	Cons
Adsorption	Organic Inorganic (heavy metals, elements) Microbes	Low cost Easy operation High efficiency	Selective removal Adsorbent fouling Disposal issues
Photocatalysis	Organic	No secondary pollution Complete degradation of pollutants	High energy required Slow reaction rate High maintenance cost
Nanomembrane	Microbes Particulates Organic Inorganic	Fewer chemicals High efficiency Low waste generation	High cost and high energy needed Waste generation Selective removal
Disinfection	Microbes	Low cost Environmentally friendly	High level of toxicity generation Potential taste and odor Limited scalability

NPs play an important role in nanotechnology for water treatment, offering innovative solutions to address water pollution challenges [14]. The integration of traditional and modern approaches highlights the dynamic nature of research and development in water treatment [15]. This collaboration addresses the increasing need for sustainable, durable, and effective water treatment solutions [16]. The NPs have been classified into two important categories: carbon nanoparticles (CNPs) and metal-oxide nanoparticles (MONPs), as shown in Figure 1.

Several review papers have been recently published regarding the role of nanomaterials in water treatment [12,17–21], the application of CNPs in water treatment [6,22,23], and the role of MONPs in water treatment [10,24]. Therefore, the efficiency of different types of CNPs and MONPs in wastewater treatment and their synthesis methods in recently published studies have been reviewed and discussed. In this review, the selection of studies

was based on their main scope and the year (about 130 studies have been published within 2020–2024). In the end, 70 papers were selected and analyzed in detail, and their results have been summarized.

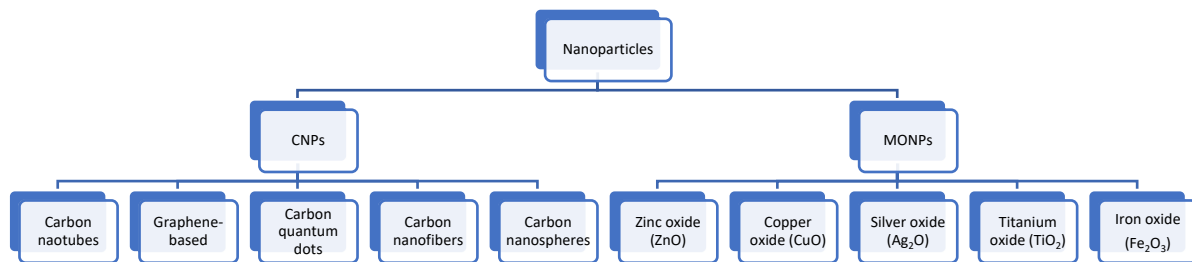


Figure 1. Different types of carbon and metal-oxide nanoparticles.

2. Adsorption Mechanism of Pollutants by Nanomaterials

As mentioned before, adsorption is a promising and popular nano-based method for wastewater treatment [25]. The effectiveness of this technique depends on the differential inter-molecular attraction between the solid absorbent and the liquid solution. The primary parameters in adsorption are the pH, temperature, dosage, ionic strength, dissolved organic matter, and initial contact time [26].

In this process, particles independently engage in the removal of pollutants as they absorb onto the outer surface of the adsorbent material, operating as a surface phenomenon. The adsorbent directly contacts the adsorbable solute or pollutants present in the water [27]. Through this phenomenon, certain adsorbate molecules adhere to the surface of the adsorbent material. This adherence creates a concentration difference in the composition of the solution between the adsorbed phase and the bulk phase, which serves as the foundation for the separation of pollutants through the adsorption process [27–29].

Chemical and physical absorptions are the two main adsorption mechanisms that influence the removal mechanism of absorbates [30]. In physical methods, the basis of the separations is the electrostatic forces between the absorbent and absorbate or Van der Waals interactions. Meanwhile, the strong interactions in chemical mechanisms could be explained by the coordination between the absorbent and solute species, acid–base bonding, and chemical covalent bonding [31,32]. Figure 2 represents different adsorption mechanisms.

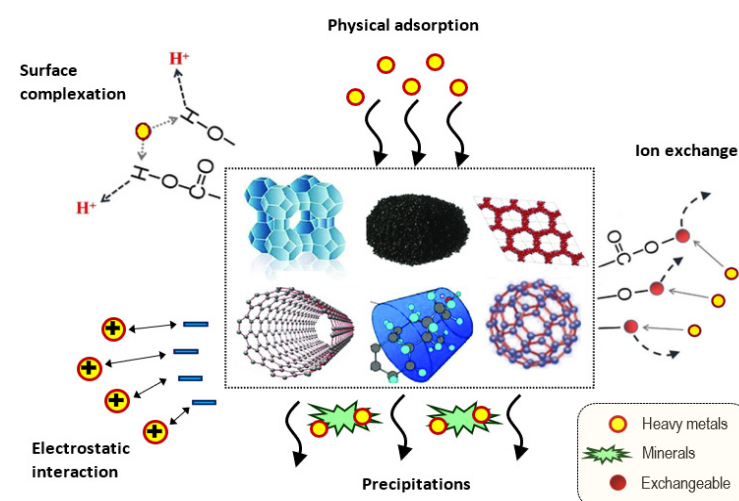


Figure 2. Schematic of different adsorption mechanisms.

Synthesis Methods of NPs

The synthesis of NPs can be divided into three primary groups: chemical, biological, and physical, as shown in Figure 3. Physical methods use pressure, thermal force, and high

energy to start transformative processes, resulting in NPs through top-down strategies [32]. These methods include energy ball milling, laser ablation, and electro-spraying, which offer precise size control, while the substantial generated waste requires critical precautions for their environmental applications in water treatment [33–35].

Physical	Chemical	Biological
<ul style="list-style-type: none"> • High-energy ball milling • Laser ablation • Laser pyrolysis • Flash spray 	<ul style="list-style-type: none"> • Sol-gel • Polyol synthesis • Chemical vapor synthesis • Microemulsion technique • Chemical vapor deposition 	<ul style="list-style-type: none"> • Bacteria-mediated • Fungi-mediated • Plant-mediated

Figure 3. Synthesis methods of NPs.

Chemical methods offer a versatile and popular approach that controls important parameters like the size, shape, and overall properties of the particles. They can be listed as the Sol-Gel Method, Microemulsion Technique, and Hydrothermal Synthesis. Chemical vapor synthesis and deposition methods operate on a bottom-up principle [36]. Because of the high temperatures, monocrystalline metal oxides would be generated by these methods. However, metallic salts can be used to reduce the metallic effects of NPs [34,37].

A new era in biological methods towards sustainable NP synthesis is providing environmentally friendly alternatives to the chemical and physical methods. The one-step bio-reduction method, employing plants, fungi, and bacteria, proves advantageous for water treatment applications [34,35]. Plant-mediated biosynthesis, utilizing plant biomolecules like enzymes, emerges as a cost-effective solution. Bacteria-mediated biosynthesis, with strains like *Escherichia coli* and *Bacillus cereus* showing diverse morphologies, provides particularly advantageous extracellular approaches [38,39]. Bacteria such as *D. radiodurans*, rich in antioxidants, are suitable for metallic NP biosynthesis. However, fungi-mediated biosynthesis efficiently uses intracellular enzymes and proteins to enhance NP stability [35,40]. These biosynthesis methods collectively signify a transformative shift towards sustainable and efficient NP production for diverse applications, including water treatment [40].

3. Carbon-Based NPs in Water Treatment

The CNPs serve as a promising part of the nanomaterial-based water treatment application due to their unique properties [41]. CNPs are nanoscale materials that have at least one dimension in the range of 1 to 100 nanometers. They have unique properties such as high surface area, lightweight, tunable properties, exceptional strength and mechanical properties, thermal and electric conductivity, and chemical stability [42]. The properties of CNPs are mainly linked to their structure, size, and functionalization. Fundamental determination and control of these factors help researchers to customize the CNPs for wastewater treatment. The versatile nature of CNPs allows them to assist in removing different types of pollutants from water [22,43].

They can be used in electrochemical processes, photocatalysis, composite materials, and disinfection for wastewater treatment. For instance, the excellent electrical conductivity of CNPs, particularly graphene, can be applied to pollutant removal via electrochemical processes. Hence, the photocatalytic and nano-enzyme properties of CNPs provide advantages for utilizing light energy and mimicking enzymatic functions in pollutant degradation [44].

These NPs exhibit high surface areas, making them effective in adsorbing a variety of contaminants, including heavy metals and organic compounds [45,46]. However, their chemical reactivity allows for transformative interactions with contaminants, leading to the degradation or modification of harmful substances. In addition, functionalized CNPs

equipped with specific chemical groups enhance their reactivity and selectivity toward targeted pollutants [47].

Based on CNP structural characteristics and unique properties, they have been classified into five groups, including CNTs, GNPs, CQDs, CNFs, and CNSs. Different types of CNPs and their synthesis methods are shown in Table 2.

Table 2. Different types of CNPs and their synthesis methods.

CNP Type	Synthesis Methods	Ref.
CNTs	<ul style="list-style-type: none"> • Electric arc discharge • CVD * • Laser ablation method 	[48]
GNPs	<ul style="list-style-type: none"> • Exfoliation and cleavage • Liquid-phase mechanical exfoliation • Intercalation of small molecules by mechanical exfoliation • CVD 	[49,50]
CQD	<ul style="list-style-type: none"> • Hydrothermal • Laser irradiation • Heating processes • Electrochemical processes • Microwave irradiation • Ultrasonication 	[51]
CNFs	<ul style="list-style-type: none"> • CVD • Electrospinning/carbonization 	[52,53]
CNSs	<ul style="list-style-type: none"> • Arc discharge process • Laser ablation • Autoclave methodology 	[54,55]

* Chemical vapor deposition.

3.1. Carbon Nanotubes (CNTs)

In recent years, CNTs have attracted great attention in wastewater treatment due to their extensive surface area and the presence of active sites. CNTs are proficient in absorbing diverse contaminants such as heavy metals, organic pollutants, and dyes. Their versatility extends to membrane technology, where CNTs can enhance filtration processes by creating membranes with nanoscale pores, improving both selectivity and permeability [56,57].

This integration is called CNT-based membranes, which have been classified into three categories, including (1) Vertically Aligned (VA-CNT), which has well-ordered cylindrical pores and the outer layer is made of polymeric using the VCD Method, (2) Mixed Matrix (MM-CNT), which consists of CNTs incorporated within polymeric or inorganic materials, and (3) Bucky Paper (BP), which refers to self-standing membranes based on the use of the highest percentage of CNTs in the membrane structure [58].

BP membranes have shown promise for diverse applications, including membrane distillation, oil–water separation, and heavy metal ion adsorption, though the issues regarding their uniform pore sizes within these membranes must be considered [59].

In addition, CNTs have shown their ability in water disinfection due to their antibacterial properties, inhibiting the growth of microorganisms. Their catalytic activity makes them suitable for advanced oxidation processes, aiding in the degradation of organic pollutants. CNTs also hold promise for addressing emerging contaminants like pharmaceuticals [60]. The significant features of CNTs make them a focal point for addressing environmental concerns and improving processes related to the purification of water [61].

The cylindrical structures of CNTs are composed of carbon atoms arranged in hexagonal patterns, forming a tubular nanostructure. These tubes have single or multiple layers

of carbon atoms, leading to the distinction between single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) [62]. The SWCNTs, featuring a diameter ranging from 0.4 to 2 nm, are formed by rolling a single graphene sheet into a cylindrical shape. In contrast, MWCNTs exhibit an outer diameter ranging from 2 to 100 nm, an inner diameter of 1 to 3 nm, and a length extending to several microns. MWCNTs are composed of two or more graphene sheets encapsulating a hollow core, a structural arrangement analogous to that of SWCNTs [63,64]. The structure of SWCNTs and MWCNTs is shown in Figure 4.

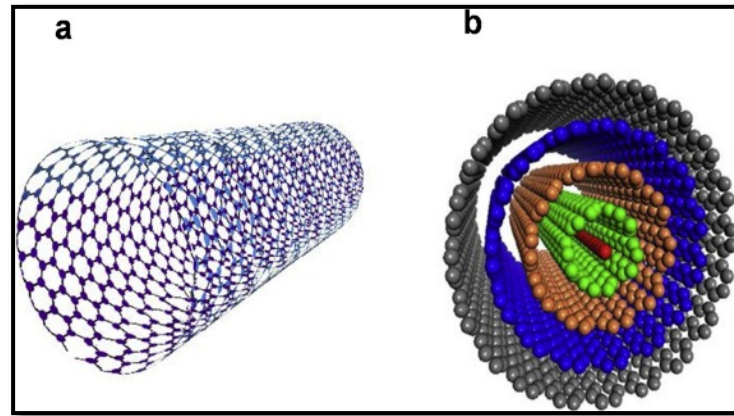


Figure 4. Structural representation of (a) SWCNTs and (b) MWCNTs. Source: Adapted from [57].

CNTs can be synthesized using different methods, including CVD, arc discharge, and laser ablation. Usually, in all synthesis methods, generated CNTs need energy and carbon sources. A carbon electrode or a combination of gas and electric current or heat serves as the carbon and energy source, depending on whether arc discharge or CVD methods are used. CVD stands out as a widely adopted method for the large-scale fabrication of CNTs globally [61]. MWCNTs can be synthesized without a metallic catalyst, while SWCNTs require mixed-metal catalysts. The method offers structural precision, but variables like chamber temperature, catalyst concentration, and hydrogen presence affect CNT structure and size [65,66].

In laser ablation for CNT synthesis, a high-energy laser beam targets a graphite source in argon at 800–1200 °C and 500 Torr pressure. The laser pulse serves as the energy source, preventing carbon soot deposition by ensuring uniform target evaporation. Subsequent laser beams break down particles into CNT structures, with transition metals typically used as catalysts. The method yields rope-shaped CNTs with diameters of 10–20 nm and lengths around 100 nm [67]. In comparison, CVD is widely used for large-scale CNT production due to its simplicity, high yield, cost-effectiveness, rapid deposition rate, and precise control over tube morphology [68].

3.2. Graphene-Based Nanoparticles (GNPs)

GNPs derived from atomically thin sp²-bonded carbon feature a hexagonal lattice structure with gas-impermeable nanopores. Controlled manipulation of graphene nanopores enables selective filtration of specific molecules, making graphene and its composites valuable in pollutant removal from wastewater [69]. Different types of GNPs, such as graphene oxide (GO), reduced graphene oxide (rGO), and graphene quantum dots (GQDs), have been used for water treatment. They are unique due to their high surface area, catalytic effectiveness, adsorption capacity, and reactivity [70]. The two-dimensional structure of graphene-based materials allows for their integration into membranes with superior mechanical strength, high permeability, and selective transport properties, enhancing water filtration processes [71]. The inherent antibacterial properties of graphene-based materials further contribute to water disinfection by inhibiting the growth of microorganisms. These materials also demonstrate catalytic activity, participating in advanced

oxidation processes for the degradation of organic pollutants [72]. Figure 5 shows different types of graphene-based materials that can be used in wastewater treatment.

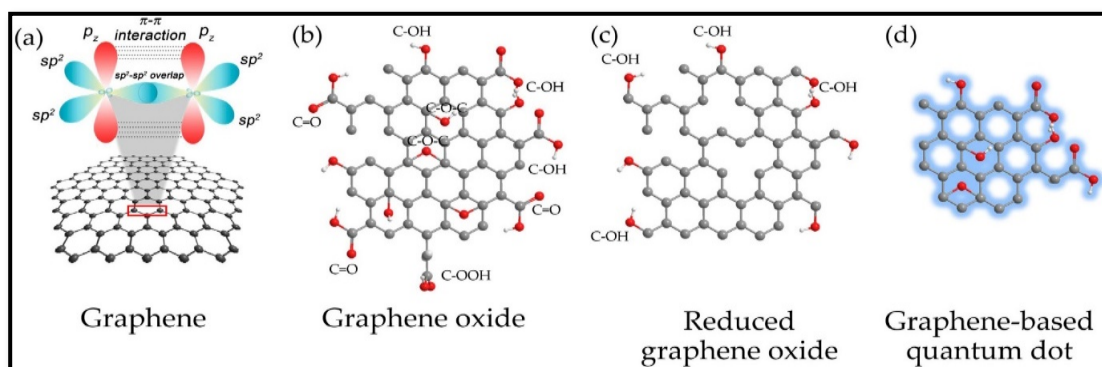


Figure 5. Different types of graphene nanomaterials: (a) graphene, (b) GO, (c) rGO, and (d) GQD. Source: [66].

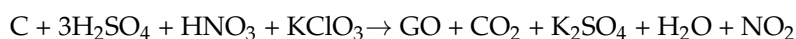
The different preparation methods used for the industrial preparation of graphene are mechanical exfoliation, electrochemical exfoliation, liquid-phase exfoliation, CVD, chemical reduction in GO, and bottom-up synthesis [73].

GO is an engineered nanomaterial with high popularity due to its high specific surface area, chemical and mechanical stability, selectivity, and tunable controlled properties. GO contains different oxygen groups (carboxyl, epoxy, and hydroxyl) that can form complexes with different organic contaminants and metal ions [74]. It can be applied in wastewater treatment via hydrogen bonding and electrostatic interaction. Several adsorption mechanisms, including precipitation and electrostatic interactions, are involved in the adsorption process of functionalized CNTs and graphene-based materials [75]. Multiple environmentally friendly approaches are used for the preparation of graphene oxide (GO). The graphene synthesis methods are the Brodie, Staudenmaier, and Hummers–Offeman methods. Hence, the improved Hummer’s method shows the most suitability for preparation due to the low toxicity level and high organization in the structure of GO [76]. The chemical reactions of these methods are shown below:

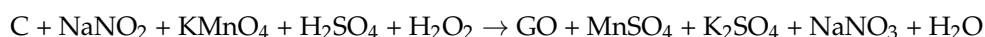
(i) Brodie method



(ii) Staudenmaier method



(iii) Hummers–Offeman method



The comparison of the Brodie and Hummers methods for the preparation of multi-layer GO shows Brodie had a less defective nature, a more homogeneous distribution of functional groups over its surface, and a smaller amount of carbonyl and carboxyl groups. Meanwhile, Hummers showed an inhomogeneous solvation and hydration with effects of inter- and intra-stratification, and the GO absorbed 3–4 times more water than the Brodie method [77].

3.3. Carbon Quantum Dots (CQDs)

Graphene-based quantum dots (GQDs) are fragments of graphene with a diameter below 20 nm that exhibit a quantum size effect. CQDs are fluorescent nanomaterials known for their strong quantum confinement effect. The synthetic approaches for GQDs

have been classified into top-down and bottom-up methods. Top-down methods involve the decomposition and exfoliation of graphite as an inexpensive and readily available bulk graphene-based material under harsh conditions. In many methods, the initial step involves converting a graphite-based starting material into graphite oxide sheets. Most commonly, a modified Hummers method is employed for this purpose [78]. Indeed, most top-down methods vary in their approaches to converting GO sheets into GQDs. These methods include microwave-assisted cutting, electrochemical cutting, ultrasonic shearing, hydrothermal cutting, and solvothermal cutting [49,50].

CQDs are typically characterized as a captivating class of carbon nanoparticles primarily composed of carbon atoms with sizes around 10 nm. They possess highly tunable photoluminescent and optoelectronic properties. In addition, the CQDs can serve as efficient photocatalysts [79]. The significant potential of CQDs in wastewater treatment arises from their attributes, such as high stability, good biocompatibility, low toxicity, high water dispersibility, low fabrication cost, and excellent photo-stability [80]. CQDs hold promise for applications in detecting heavy metal ions [81], removing both organic and inorganic pollutants [82], and facilitating the photocatalytic degradation of wastewater pollutants [83].

3.4. Carbon Nanofibers (CNFs)

Carbon nanofibers (CNFs) are nanometer-sized filaments with diameters ranging from 3 to 100 nm, composed of stacked graphene layers oriented to the fiber axis. This material is commonly categorized into three types based on the angle between the graphene layers and the growth axis: parallel (angle: 0°), fishbone ($0^\circ < \text{angle} < 90^\circ$), and platelet (angle: 90°). CNFs exhibit a turbostratic nature, characterized by an average spacing between graphene layers of approximately 0.34 nm, closely resembling the interlayer spacing in graphite (0.335 nm) (Figure 6).

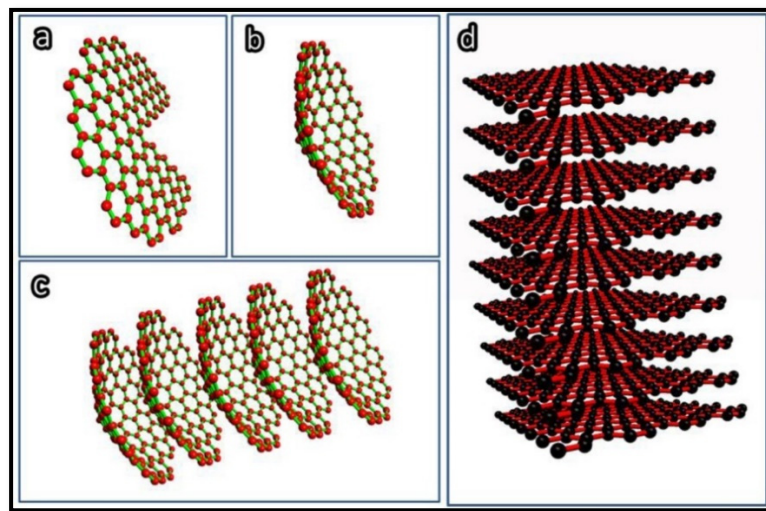


Figure 6. (a–c) Formation of a cup-stacked CNF structure and a (d) platelet CNF structure. Source: adapted from [84].

CNFs are primarily synthesized through two main methods: CVD and electrospinning/carbonization. The synthesis processes are influenced by several parameters that provide flexibility in tailoring the properties of the CNFs. The final characteristics of the CNFs are significantly influenced by the choice of carbon precursor and the reaction conditions. Generally, high temperatures exceeding 500°C are required for the synthesis [85].

CNFs exhibit promising potential for water treatment applications due to their large surface area and unique properties. They can be functionalized for enhanced adsorption, effectively removing pollutants like heavy metals and organic compounds from water. CNFs can serve as a catalyst support, contributing to electrocatalytic processes for advanced

oxidation. Their integration into membranes enhances filtration capabilities, offering high permeability and selectivity [86]. Additionally, CNFs can be utilized in electrochemical processes, such as capacitive deionization for ion removal. Some types of CNFs possess antibacterial properties, aiding in water disinfection. Despite their potential, ongoing research is crucial to optimize their performance and scalability and address environmental and health considerations associated with nanomaterials [87,88].

3.5. Carbon Nanospheres (CNs)

Carbon nanospheres (CNs), or fullerenes, refer to spherical carbon particles without a specific molecular structure. They can be solid or hollow. These vary in composition and may include amorphous carbon or graphite-like structures. They are not limited to a specific number of carbon atoms in a closed cage. They can be classified into three categories: the C_n family and carbon onions (2–20 nm), carbon nanosized spheres (50 nm to 1 mm), and carbon beads (one to several microns) [89]. Carbon onions, according to Inagaki's textural classification, are viewed as concentric, nested hyperfullerenes, with C₆₀ being the smallest [90]. The unique structure of carbon onions, with a large surface-to-volume ratio, contributes to their stability by eliminating dangling bonds.

CNs can be fabricated via the arc discharge process, laser ablation, and autoclave methodology. Carbon sphere-derived materials offer a promising alternative to activated carbon in the water treatment industry. When hydroxylated, these materials exhibit enhanced contaminant trapping capacity attributed to an abundance of surface sites, variable specific surface area, and favorable surface charging [91]. The versatile applications of carbon spheres and their functionalized counterparts extend across various fields, with significant relevance in water treatment [54,55].

Fullerenes are a family of carbon allotropes with molecules in the form of a hollow sphere, tube, or ellipsoid that is composed entirely of carbon. Fullerenes have been extensively used for photocatalytic wastewater treatment, including disinfection and pollutant degradation [92]. The most well-known fullerene is C₆₀, a molecule consisting of 60 carbon atoms with low solubility and dispersibility in water and easy agglomeration [93,94].

Their synthesis methods include arc discharge, laser ablation, and solvent-based methods. Fullerenes are suggested as a foundation for advancing technologies that harness nanomaterials for enhanced oxidation and disinfection, improved membrane processes, superior adsorbents, and surfaces resistant to biofilm formation [95]. Their nanostructures with high adsorption capacities revealed their importance in the field of membranes [96]. Table 3 shows recent studies on the removal of different pollutants using different types of CNPs.

Table 3. Recent studies on the removal of different pollutants from water treatment using CNPs.

Type of CNPs	Synthesis Methods	Pollutant Type	Surface Area(m ² /g)	Optimum Condition	Adsorption Capacity (mg/g)	Removal (%)	Ref.
MWCNTs-KOH@Ni	NA	Pb (II)	1242	pH: 5.5	481	91.2 88.5 80.6	[97]
		As (V)		T: 303 K	415.8		
		Cd (II)		30 min	440.9		
rGO hydrogel (rGOH)	Improved Hummer's method	Pb (II)	553.69	pH: 4	2503.62	80	[98]
		Cd (II)		T: 298 K	1185.27		
				5 min			
GO-Gd ₂ O ₃ nanocomposite	Hummer's method	Pb (II)	2.757	pH: 4	158.73	99	[99]
				T: 298 K			
				1080 min:			

Table 3. Cont.

Type of CNPs	Synthesis Methods	Pollutant Type	Surface Area(m ² /g)	Optimum Condition	Adsorption Capacity (mg/g)	Removal (%)	Ref.
rGO–Starch composite (rGO/WS)	Improved Hummer's method	Cu (II)	406.40	pH: 8 24 min	542.01	90.34	[100]
MWCNTs	CVD	As (V) Mn (VII)	1250	pH: 6 50 °C 60 min	200 192	NA	[101]
CNs	CVD	Ibuprofen	359	pH: 6 T: 25 °C 90 min	356.899	NA	[102]
CQD-CNTs	One-step CVD	Methylene blue	324.4	pH: 6, T: 313 K 5 min	299.4	99.5	[103]
MWCNTs Cellulose beads	Solvent-free	Methylene blue	NA	pH: 7 25 °C 1.07 min	285.71	97.05	[104]
Fe@MWCNTs	NA	Azorubine	59.2	pH: 5 T: 24–26 °C 30 min	NA	95	[105]
MWCNTs	CVD	Ismate violet 2R	181.99	pH: 4 T: 30 °C 120 min	76.92	88.2	[106]
MWCNTs	Arc discharge	Methyl orange Rhodamine B	24 237	120 min	NA	16 60	[107]
Co-N@CNTs	Two-step carbonization method	Oxalic acid	125.5	pH: 4.5	5	92	[108]
MWCNT–amino acid	NA	Ibuprofen	154.5	pH: 4 Room T	11.8	98.4	[109]
Co@CoO/NC	One-step annealing method	Rhodamine Tetracycline	277.6	pH: 8 60 min	679.56 385.60	98 99	[110]
FMWCNTs	CVD	Total organic carbon	831.80	pH: 7 T: 34 °C 49 min	260	93.6	[111]
(MWCNTs)–SiO _{2.5} composite	Sol-gel method	Toluene	729	30–60 °C 10–30 min	50.28	73	[112]
GO	Improved Hummer's method	Sodium diclofenac	NA	pH: 6.2 25–45 °C 300 min	128.74	74	[113]
CNFs	Solid-phase microextraction	Alkylphenols	NA	Room T 5 min	NA	73.58–85.76	[114]

NA: not available; Room T: room temperature.

4. Metal-Oxide Nanoparticles (MONPs) in Water Treatment

Nanomaterials exhibit shape-dependent optical and electronic characteristics, and their small particle sizes are responsible for a large surface-to-volume ratio [115]. Among nanomaterials, MONPs stand out as the most diverse, consisting of distinctive characteristics such as a significant surface area, high adsorption capacity, increased catalytic activity, high selectivity, and increased reactivity [10,116]. The unique properties of MONPs are determined by their crystalline structure. This arrangement of metal and oxygen atoms influences key characteristics such as reactivity, conductivity, and size, making it crucial to understand and manipulate for tailored applications such as water treatment [117]. The efficiency of MONPs in activities like antibacterial actions and dye removal from wastewa-

ter is dependent on various factors, including morphological configuration, stability, and aggregation capabilities [35]. These distinctive magnetic properties, coupled with the inherent reactivity associated with their crystalline structures, make MONPs ideal candidates for pollutant removal from wastewater [40,118–120]. Figure 7 shows the adsorption mechanism using magnetic nanosheets.

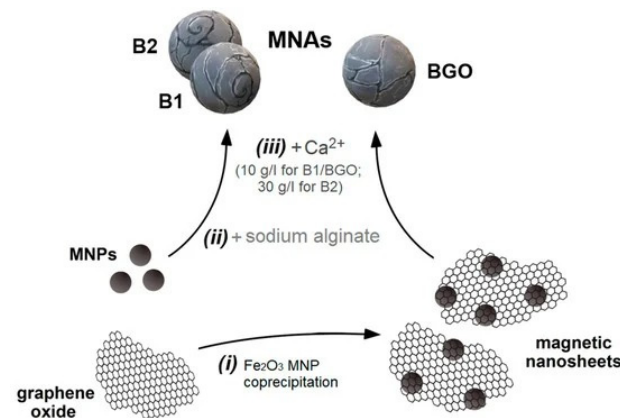


Figure 7. Schematic of the adsorption mechanism using magnetic nanosheets. Source: [121].

There are several types of MONPs, including aluminum oxide, copper oxide, zinc oxide, cerium oxide, iron oxide, manganese oxide, and titanium oxide [10,36,122–124]. In 2021, Naseem and Durrani [10] reviewed the role of important MONPs in wastewater treatment and found that ZnO is the most used MONP in wastewater treatment, followed by CuO and TiO₂. Therefore, in this section, recent studies about the applications of different MONPs in wastewater treatment in the last three years have been summarized.

4.1. Zinc Oxide Nanoparticles

ZnO NPs are suitable candidates for wastewater treatment because of their unique stability and ability to generate reactive oxygen bonds, which accelerate the degradation of pollutants [125]. ZnO NPs stand out as superior photocatalysts due to their wide bandgap for efficient absorption of light and generation of electron–hole pairs [126].

In addition to these photocatalytic characteristics, ZnO NPs have a large surface area for better adsorption of different pollutants [127]. This dual functionality enhances their effectiveness in water treatment processes, as they can efficiently capture and remove pollutants through adsorption in addition to photocatalytic degradation [128]. Recent studies by Norbert et al. [119], El Golli et al. [120], and Biswal et al. [121] proved the effectiveness of ZnO NPs in the textile industry for dye removal from wastewater, as summarized in Table 4.

Table 4. Recent studies on the application of ZnO NPs in water treatment.

Nanomaterial	Modification	Synthesis Method	Pollutant Type	Mechanism of Action	Removal Time	Removal Rate (%)	Ref.
ZnO NPs	Spherical NPs with no modifications	Co-precipitation	Methyl orange (MO) and amaranth (AM)	Adsorption	120 min	MO: 60 AM: 78	[129]
ZnO nanorods	Fabrication on zinc and titanium foil	Electrochemical anodization	Congo red and methyl orange	Adsorption and photocatalytic degradation	75 min	96	[130]
ZnO nanorods	ZnO thin film	Co-precipitation	Methylene blue dye (MB)	Photocatalytic degradation	120 min	69 to 73	[131]
ZnO NPs	Ni tubular thin films	Pulse electro deposition	Textile dyes	Photocatalytic degradation	60 min	91.21	[132]
ZnO NPs	Hydrogel composite	Bio-reduction	<i>Escherichia coli</i>	Adsorption	35 min	70	[133]

4.2. Copper Oxide Nanoparticles

The application of Cu oxide nanoparticles is very successful in wastewater treatment due to several factors, such as their small size, low production costs, large surface area, and inherent synthesis availability [134]. Cupric oxide (CuO) and cuprous oxide (Cu₂O) are the two basic copper oxides most frequently used in industrial applications. The nano form of these oxides functions as effective adsorbents in the field of wastewater [36]. CuO NPs have a remarkable maximum fluoride adsorption capacity of 3152 mg. This indicates that they have a considerable capacity to remove a substantial amount of fluoride from wastewater. CuO NPs exhibit endothermicity and spontaneity in their thermodynamic adsorption behavior, which highlights their applicability in wastewater treatment processes [36,135]. Moreover, the inherent redox activity of Cu nanomaterials enables participation in chemical reactions that aid in removing or transforming pollutants [136].

Recently, Eid et al. [127] studied the efficiency of using biosynthesized CuO NPs in the process of treating tanning wastewater from the textile industry. Tanning wastewater exhibited a significant decrease in its physicochemical parameters when it was in an ideal setting. There was a significant decrease of 95.2%, 86.7%, 91.4%, 87.2%, and 97.2% in total suspended solids (TSSs), total dissolved solids (TDSs), chemical oxygen demand (COD), biological oxygen demand (BOD), and conductivity, respectively. The studies by Rahdar et al. [128], Baylan et al. [129], and Prajapati and Mondal [130] investigated the effectiveness of CuO nanoparticles for the removal of pollutants from wastewater (Table 5).

Table 5. Recent findings on the application of CuO NPs in water treatment.

Nanomaterial	Modification	Synthesis Method	Pollutant Type	Mechanism of Action	Removal Time	Removal Rate (%)	Ref.
CuO NPs	NA	Co-precipitation	NO ₃ [−] ions	Adsorption	120 min	66.9–71.56	[137]
CuO NPs	NA	Simple precipitation	Acrylic acid	Adsorption	180 min	75–78	[138]
CuO NPs	NA	Bio-reduction	Co, Pb, Ni, Cd, Cr (VI)	Adsorption	20 min	Co: 73.2, Pb: 80.8, Ni: 72.4, Cd: 64.4, Cr (VI): 91.4	[139]
CuO NPs	Ag doped	Bio-reduction	Cr and Cd	Adsorption	72 h	Cr: 2.11 Cd: 2.91	[140]
CuO NPs	Loaded into nano porous activated carbon	Co-precipitation	MB dye	Adsorption	180 min	93.51	[141]
CuO NPs	NA	CuO NPs	Ni ²⁺ , Cr ³⁺ ions	Adsorption	30 min	Ni ²⁺ , Cr ³⁺	[142]

4.3. Silver Oxide Nanoparticles

Silver nanoparticles (AgNPs) are capable of degrading dyes and organic pollutants by adsorption and catalytic/photocatalytic activity [143]. They have a narrow band gap (HOMO to LUMO) between 1.2 and 1.6 eV and behave like p-type semiconductors. This narrow bandgap helps them absorb the full range of solar light and works as an excellent photocatalytic agent to break down organic pollutants in water [144]. In addition, their specific surface area affects the effectiveness of silver ions that are released from their surfaces. Xu et al. [137] and Kadam et al. [138] achieved 99% of malachite green dye and 97.57% of MB dye removal using AgNPs, respectively.

Ag₂O NPs can be produced by a variety of techniques: solid phase, like energy ball milling and physical pulverization of the metal; gas phase, like electrochemical processes and evaporation/vapor condensation; and liquid phase, like chemical reduction and irradiation-assisted methods [36]. Ag₂O NPs can be customized for specific applications using a variety of synthesis techniques, utilizing their special qualities for environmental remediation. Green synthesis is a novel trend in Ag₂O nanomaterials synthesis where the sustainable nature and uniformity of the nanostructures are observed compared to conventional methods [145,146]. Table 6 summarizes the applications of Ag₂O NPs in the field of water treatment.

Table 6. Recent findings on the application of Ag₂O NPs in water treatment.

Nanomaterial	Modification	Synthesis Method	Pollutant Type	Mechanism of Action	Removal Time	Removal Rate (%)	Ref.
Ag ₂ O nano fibers	None	Bio-reduction using cauliflower waste	MB dye	Photocatalytic degradation	150 min	97.57	[146]
Ag ₂ O nano fibers	AgO loaded polyacrylonitrile membrane	In situ redox reaction	MB dye and Pb ²⁺	Photocatalytic degradation	15 min	MB dye 99.5 and Pb ²⁺ 99.7	[147]
Ag ₂ O NPs	None	Bio-reduction using <i>H. hirsuta</i> plant extract	MB dye	Photocatalytic degradation	35 min	88.6	[145]
Ag ₂ O NPs	None	Ion exchange	Non azo dye (MO, MB, RhB)	Photocatalytic degradation	20 min	MO 90.2, RhB 96.5, and MB 99.5	[148]
Ag ₂ O NPs	+ (Ag ₂ O-Mn-NPs)	Co-precipitation	Malachite green (MG) dye	Photocatalytic degradation	60 min	99	[149]

4.4. Titanium Oxide Nanoparticles

Titanium oxide (TiO₂) nanoparticles have been studied in recent years because of their remarkable photocatalytic activity, chemical and biological stability, strong photostability, and reasonable cost [36]. TiO₂ NPs are a great catalyst for the breakdown of numerous pollutants, including pesticides, organic compounds, heavy metals, arsenic, and polycyclic aromatic hydrocarbons, present in wastewater [150]. TiO₂ NPs have an amazing ability to release reactive oxygen species (ROS) when exposed to UV light, which starts the breakdown of pollutants. Interestingly, TiO₂ NPs produce hydroxyl radicals when exposed to UV radiation ($\lambda < 400$ nm), which increases their capacity to destroy pollutants by interfering with the structures and operations of cells [151]. TiO₂ NPs commonly exist in different crystalline forms, such as anatase, rutile, and brookite, each exhibiting distinct photocatalytic activities (Figure 8) [152,153].

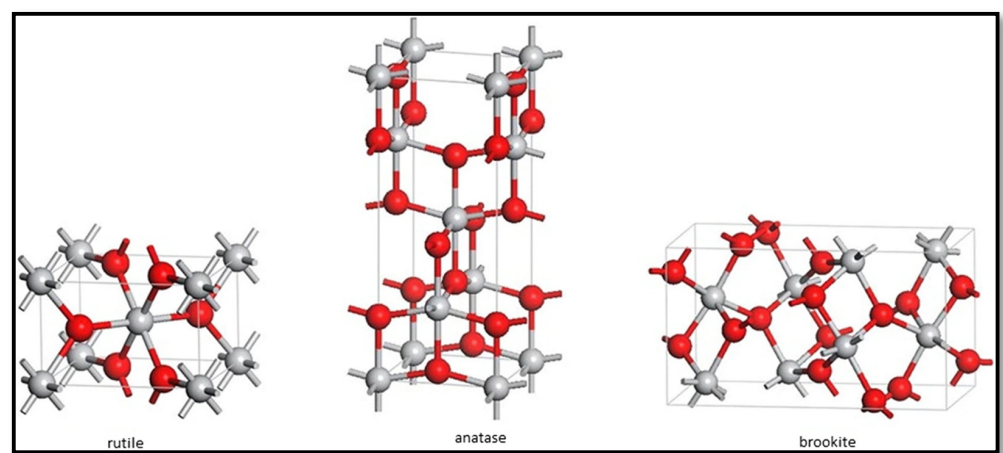


Figure 8. Different crystalline structures of TiO₂ nanomaterials: anatase, rutile, and brookite. The red ball represents the Ti²⁺ ion, and the white ball is O₂[−]. Source: [154].

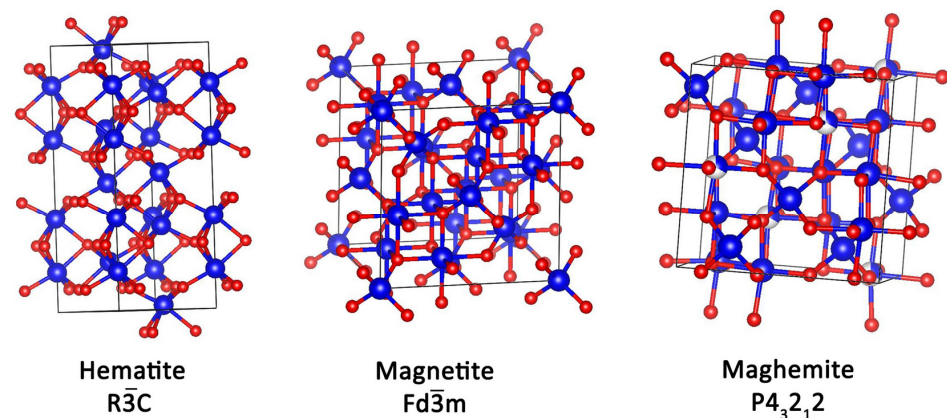
Langa et al. [149] achieved a combined dye removal effect (CR dye 87%) and a strong antibiotic degradation effect (SMX 82% and CIP 94.6%) from non-doped simple TiO₂ NPs. Several recent studies reported the ability of TiO₂ NPs in wastewater treatment by photocatalytic degradation and adsorption, which are summarized in Table 7.

Table 7. Recent findings on the application of TiO₂ NPs for water treatment.

Nanomaterial	Modification	Synthesis Method	Pollutant Type	Mechanism of Action	Removal Time	Removal Rate (%)	Ref.
TiO ₂ nano fibers modified	Diethylenetriaminepentaacetic acid functionalized DTPA/MWCNT/TiO ₂	Electrospinning	Oil emulsions	Adsorptive removal	15 min	97.4 ± 1	[155]
TiO ₂ NPs	None	Hydrothermal synthesis	MB dye	Photocatalytic degradation/Anti-bacterial action	120 min	92	[156]
TiO ₂ NPs	None	Bio-reduction using <i>Monsonia burkeana</i> plant	MB dye	Photocatalytic degradation	120 min	85.5	[157]
TiO ₂ NPs	None	Bio-reduction using <i>Sutherlandia frutescens</i> plant extraction	CR dye Antibiotics ciproflaxin and sulfamethoxazole	Photocatalytic degradation	CR dye and antibiotic: 120 min	CR dye: 87, SMX: 82, and CIP: 94.6	[158]
Doped TiO ₂ NPs	Ag surface modification	Plasma-liquid synthesis	DPPH radical	Photocatalytic degradation	120 min	31–70	[159]
Coated TiO ₂ NPs	Ag NP coated	Sol-gel method	MB dye	Photocatalytic degradation	120 min	90.9	[160]

4.5. Iron Oxide Nanoparticle

Iron oxide nanoparticles (Fe₂O₃ NPs) have received significant attention recently due to their unique properties, which include super-paramagnetism, a large surface area, a high surface-to-volume ratio, high stability, strong adsorption capacity, low production cost, and fast separation methods [115]. Each crystalline form exhibits unique magnetic behaviors, with magnetite showcasing strong magnetic properties (ferromagnetism), hematite displaying nonmagnetic properties despite having magnetic elements within them (antiferromagnetism), and maghemite falling in between [161]. These Fe₂O₃ NPs stand out from other NPs in environmental remediation due to their distinct magnetic properties [162,163]. Figure 9 shows three types of Fe₂O₃ that are commonly recognized as hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), and magnetite (Fe₃O₄) [115].

**Figure 9.** Crystal structures of hematite, magnetite, and maghemite. Source: [164].

Additionally, Fe₂O₃ NPs are useful in the photocatalytic degradation of dyes. Sheikholeslami et al. [157] synthesized γ -Fe₂O₃ NPs using the co-precipitation method, with slight modifications, to enhance their efficacy in the photocatalytic degradation of BTEX in wastewater. Their study revealed impressive results, achieving a maximum degradation efficiency of 95% within 5 days. Moreover, under UV light and visible light irradiation, the degradation efficiency reached 97% within 90 min, highlighting the potential of these magnetite NPs for rapid and effective remediation of BTEX [165]. Recently, Xu et al. [159] reported the strong adsorptive removal of Pb²⁺ ions from wastewater using sulfur-doped

magnetic Fe₃O₄ NPs, achieving approximately 80% removal. Table 8 summarizes recent findings on organic dye and toxic metal ion removal using iron oxide NPs.

Table 8. Application of Fe₂O₃ NPs in wastewater treatment.

Nanomaterial	Modification	Synthesis Method	Pollutant Type	Mechanism of Action	Removal Time	Removal Rate (%)	Ref.
α -Fe ₂ O ₃	Hematite was selected over other crystalline structures	Bio-reduction	COD, TDS, TSS	Photocatalytic degradation	8 h	COD: 82.8 TDS: 47.6 TSS: 75.7	[166]
Fe ₂ O ₃	CuO-CeO ₂ -Fe ₂ O ₃ nanocomposite	Reduction	Red 60 textile dye	Adsorption	3 h	77	[167]
α -Fe ₂ O ₃	None	Bio-reduction	Yellow RR dye	Photocatalytic degradation	6h	76.6	[168]
CMC-Fe ₃ O ₄	Carboxymethyl cellulose-immobilized	One-step high-gravity precipitation	Pb ²⁺	Adsorption	12 min	68.4	[169]
Fe ₃ O ₄	Sulfur	Micro emulsion	Pb ²⁺	Adsorption	24 h	~80	[170]

5. Cost Analysis of CNPs and MONPs

The cost of nanoparticle (NP) preparation is a critical factor in wastewater treatment that requires careful evaluation. The associated cost of applying nanoparticles in wastewater treatment can be classified into three important categories: the cost of raw materials, the scale of production, and the cost of NP synthesis and preparation [10]. The details of nanomaterials cost are shown in Figure 10.

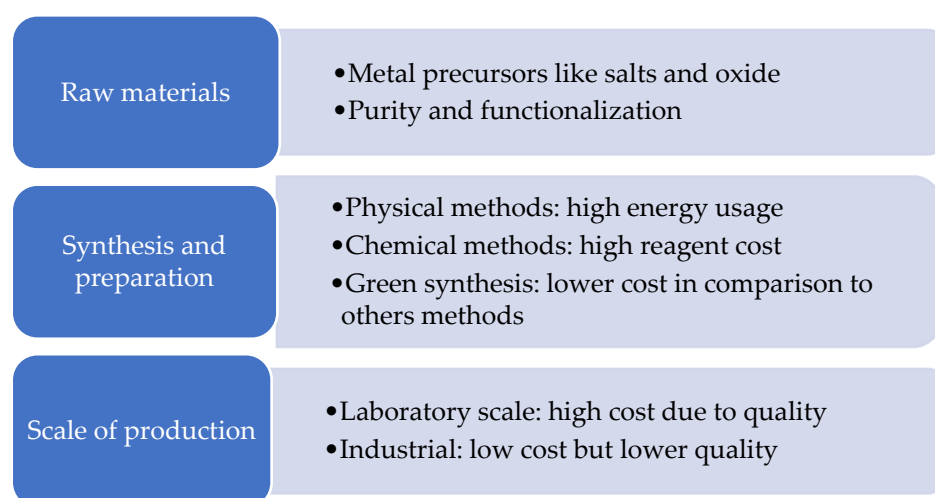


Figure 10. Different cost allocations of nanomaterials in the wastewater treatment process.

As recently reviewed by GadelHak et al. [171], the cost of adsorbent production depends on raw material, transportation, used chemicals, and energy consumption. They found that energy costs contributed to 91% of the total production cost. The cost of producing and utilizing a specific adsorbent is a crucial factor considered by designers and engineers operating large-scale systems. Then, the selection of adsorbents for large-scale applications is based on the overall cost of pollutant removal, not solely on their adsorption capacity.

Researchers are actively exploring ways to reduce these costs by developing innovative preparation methods or utilizing readily available materials. As reported by Mpongwana and Rathilal [172], one potential solution is the use of plant-based materials for NP production. This approach highlights the promise of biological methods as a sustainable and cost-effective alternative. In addition, studies indicate that recycling NPs could further lower expenses, offering an economically and environmentally viable solution to minimize reliance on freshly produced nanoparticles.

6. Challenges and Limitations

Despite the advances in employing carbon-based or metal-oxide nanomaterials in treating wastewater, a few challenges and limitations need further evaluation. Understanding the behavior, consequences, and long-term ecological effects of nanoparticles in aquatic environments is critical. Studies have shown that nanoparticles can undergo aggregation, dissolution, or chemical transformations in water, altering their properties and potential toxicity [173]. Establishing robust monitoring systems and risk assessment protocols is essential to ensure their safe application and disposal, minimizing adverse environmental consequences [174].

Additionally, nanomaterials may degrade under specific conditions, reducing their efficacy in wastewater treatment. For example, photocatalytic nanoparticles like TiO_2 can lose activity due to fouling or changes in water chemistry. Developing advanced nanomaterials or applying surface modifications could improve durability and functional performance under harsh conditions. Addressing these challenges requires innovative research to enhance the stability and resilience of nanomaterial-based systems. Furthermore, the potential environmental release of nanomaterials during wastewater treatment operations raises concerns about their impact on aquatic ecosystems and human health [175]. Lastly, the other crucial issue limiting the usage of CNTs is their high cost in comparison to traditional adsorbents for full-scale water treatment applications. To solve this issue, it is necessary to carry out efficient and economical synthesis methods to modify and functionalize CNT materials to produce them on a wide scale.

Most of the research work on carbon nanotube adsorbents is completely focused on laboratory experiments. To fully exploit the potential of CNTs and CNT membranes, studies on long-term performance, real wastewater, and the transition to large-scale applications are mandatory. In this direction, CNT production costs play a predominant role, and the annual production price cut recently experienced can support the design and investigation of low-cost methods in the next few years [176].

7. Conclusions and Future Perspectives

In this review, the recent advances in the application of carbon-based (CNTs, GNPs, CQDs, CNFs, CNs) and metal-oxide nanoparticles (ZnO , CuO , Ag_2O , TiO_2 , Fe_2O_3) in wastewater treatment have been evaluated. Based on reviewing the literature, the following conclusion can be drawn:

- CNTs, GNPs, and CQDs exhibit unique properties in water treatment processes. These materials, with their high surface area, adsorption capabilities, and catalytic properties, contribute to the removal of diverse contaminants, including heavy metals and organic compounds. CNTs, with their extensive specific surface area, show proficiency in adsorbing contaminants and enhancing filtration processes. Graphene-based materials, such as GO and rGO, contribute to water purification through their unique structural and catalytic properties. CQDs showed their excellence in removing heavy metals from wastewater.
- Although the studies for CNFs and CNs are rare, they demonstrated high potential for water treatment due to their large surface area and unique properties. CNFs can be functionalized to enhance adsorption capacity in electrochemical processes, while CNs offer an alternative to activated carbon with enhanced contaminant trapping capacity.
- The study of the process and mechanism of CNT functionalization is very important. Generally, several factors, including surface chemistry, surface charge, functional groups, the surfactants' pore properties, and the altered chemical structure, control the adsorption of pollutants by CNTs.
- The experimental parameters, including temperature, pH, and adsorbent/adsorbate concentration, have an impact on the effectiveness of the pollutant removal rate. Based on the findings, functionalization has consistently increased the efficiency of CNTs in comparison with unfunctionalized CNTs. In the pH range of 4–6, most of the pollutants exhibited a greater affinity for the carbonaceous adsorbents and functionalized CNTs.

From the findings in Table 2, it can be concluded that the removal rate of pollutants using CNPs was in the range of 75 to 98% removal within 2 h.

The diverse modifications and applications of MONPs highlighted their potential in water treatment processes. Each type of MONP is capable of the adsorption of different pollutants based on their properties as listed below:

- ZnO NPs exhibit superior photocatalytic properties, making them effective in different types of dye reduction. The range of dye removal using different types of ZnO nano-materials was from a minimum of 60% for methyl orange in 120 min to a maximum of ~97% for Rhodamine blue dye in 75 min.
- CuO NPs exhibit remarkable adsorption capacities for various contaminants, including heavy metals, with a minimum removal of 64.4% for Cd^{2+} and a maximum removal of 91.4% for Cr^{4+} .
- Ag_2O , as a photocatalytic agent, exhibits excellent capacity for breaking down organic pollutants and potential antimicrobial properties. The synthesized Ag_2O nanofibers from cauliflower waste had a 97.57% removal of MB dye in 150 min, demonstrating cost-effective and environmentally friendly materials for efficient pollutant removal.
- TiO_2 NPs have extensively shown their photocatalytic activity, chemical stability, and low cost. They exhibit impressive capabilities in the breakdown of pollutants, including pesticides and organic compounds, through the release of reactive oxygen species. Ag-coated TiO_2 NPs exhibited a notable 90.9% photocatalytic degradation of MB dye in 120 min, showing enhanced stability and reusability compared to TiO_2 .
- Fe_2O_3 nanoparticles with different crystalline forms, such as hematite and magnetite, stand out for their unique magnetism, making them effective adsorbents for heavy metal ions and excellent candidates for photocatalytic degradation. For instance, $\alpha\text{-Fe}_2\text{O}_3$, bio-reduced by *Aspergillus carbonarius*, exhibited 82.8%, 47.6%, and 75.7% reduction in COD, TDS, and TSS in textile plant wastewater, respectively.

Recent studies reported the effectiveness of these nanomaterials in removing various contaminants, including dyes, heavy metals, and bacteria, contributing to the advancement of environmentally friendly and efficient treatment technologies. As the field of nanotechnology continues to evolve, ongoing research and development will likely yield further insights into optimizing the performance of these nanomaterials and addressing challenges such as stability, reusability, and potential toxicity. The promising results presented in this overview suggest that MONPs hold great potential for shaping the future of water treatment technologies. Using green synthesis methods and surface modifications further enhances the efficiency and sustainability of these nanomaterials.

To ensure the development of sustainable and effective water treatment solutions in the future, research on nanomaterials must be conducted to improve their performance, scalability, and environmental considerations. As nano adsorbents, CNTs have demonstrated a great deal of promise in the removal of pollutants from wastewater. However, additional research is required to evaluate the efficiency of CNTs in treating actual and industrial wastewater samples under long-term operating circumstances.

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